SURFACTANT CHEMICALS COMPANY
Innovative Surface Chemistry

PROJECT PHEONIX: THE ADRENALINE ® SURGE – 3

ADRENALINE ® N4960 vs ® N4950: PYRIPROXYFEN 18.8%EW

GENERAL CHAPTER – EWC10 – R3 – 10 Mar 2024

PROJECT PHEONIX: THE ADRENALINE ® SURGE

In a groundbreaking comparative study, the performance of ADRENALINE ® N4960 was evaluated against its predecessor, ADRENALINE ® N4950, within EW (Emulsifiable Concentrate) formulations and Suspo Emulsion (SE) formulations. Both surfactants, renowned for their polymeric nature, were scrutinized to determine the advancements brought by the newer molecule. The results were compelling: ADRENALINE ® N4960 emerged as a superior innovation, showcasing significantly lower viscosity, which translates to enhanced handling and a better pour point. This improvement not only facilitates easier application but also ensures more efficient processing. Additionally, the slightly higher molecular weight of ADRENALINE ® N4960 contributes to its exceptional stability and anchoring capabilities, making it a robust choice for various formulations. Beyond its technical merits, ADRENALINE ® N4960 also proves to be more cost-efficient, offering economic advantages without compromising on performance. This study underscores the innovative leap represented by ADRENALINE ® N4960, setting a new benchmark in the realm of polymeric surfactants and paving the way for more efficient and stable EW formulations.

SAMPLING AND DELIVERABLES

ADRENALINE® Polymeric Surfactants are renowned for their colloidal stabilization capabilities, crucial in agricultural formulations. These surfactants exhibit slower migration kinetics to the colloidal interface compared to monomeric surfactants, necessitating optimized processing times. The colloidal interface, where dispersed particles interact with the continuous phase, benefits from precise shear mixing protocols. Various shear mixing durations were evaluated to ensure optimal surfactant distribution and interface migration. This optimization is vital for achieving superior colloidal stability, enhanced shelf life, and improved formulation performance.

Sampling points for testing and deliverables are defined in below table:

Sampling points	Tests to be performed
After normal mixing oil phase into water phase	Droplet size. Distribution D_{90} and D_{50} viscosity (cPs), temperature and torque
After normal mixing emulsion stability (T_0)	Emulsion test (T_0), 30min, 2hrs, 24hrs and 24.5hrs
After 5min high shear@15000RPM	Droplet size distribution D_{90} and D_{50}
After 5min high shear, emulsion stability (T_5)	Emulsion test (T_5), 30min, 2hrs, 24hrs and 24.5hrs
After 10min high shear@15000RPM	Droplet size distribution D_{90} and D_{50}
After 10min high shear, emulsion stability (T_{10})	Emulsion test (T_{10}), 30min, 2hrs, 24hrs and 24.5hrs
After 15min high shear@15000RPM	Droplet size distribution D_{90} and D_{50}
After 15min high shear, emulsion stability (T_{15})	Emulsion test (T_{15}), 30min, 2hrs, 24hrs and 24.5hrs
Recovery	% recovery after bead milling
Viscosity after high shearing	Viscosity, temperature and torque
After maintaining the final viscosity	Droplet size distribution D_{90} and D_{50} Viscosity, temperature and torque, density, pH 1%, pH 5%
Emulsion stability of final sample (T_F)	Emulsion test (T_F), 30min, 2hrs, 24hrs and 24.5hrs
Other physical tests	Density, pH 1% solution, pH 5% solution
Post stability testing	
Physical form	To check the physical status (phase separation, sedimentation, oil etc.)
Droplet size and other tests	Droplet size distribution D_{90} and D_{50}, emulsion stability, viscosity, temperature and torque, density, pH 1%, pH 5%

FORMULATION

A constant recipe used for all trials except the Surfactant Combinations and % Dosages varies in all trials.

PYRIPROXYFEN 18.8%EW (PROJECT PHEONIX: N4950 VS N4960) DATED:07-09-22		
PYRIPROXYFEN 18.8%EW (batch size: 500gms)		
	Formulation code: RF-10962 vs RF-10963	%w/v
Pyriproxyfen tech.	Active, 95%	19.79
ADRENALINE ® N5050	Polymeric surfactant	2.00
ADRENALINE ® N4950/4960	Polymeric surfactants	2.00
Monoethylene glycol	Antifreeze agent	6.00
Antifoam	Silicone antifoam	0.10
Xanthan gum 3% slurry	Structuring agent and biocide	15.00
Xylene	Solvent	25.00
Water	Continuous phase	30.85
Total		**1 ltr**
Oil phase		%w/v
Pyriproxyfen tech.	Active, 95%	19.79
ADRENALINE ® N4950/4960	Polymeric surfactant	2.00
Xylene	Solvent	25.00
Total		**46.79**
Water phase		%w/v
ADRENALINE ® N5050	Polymeric surfactant	2.00
Monoethylene glycol	Antifreeze agent	6.00
Antifoam	Silicone antifoam	0.10
Water	Continuous phase	30.85
Total		**38.95**
Structuring agent		
Xanthan gum 3% slurry	Xanthan gum 3% + Biocide 1.5% + Water 96.5%	15.00

SURFACTANT COMBINATIONS AND % DOSAGES USED

Following Surfactant combinations and % dosages were used for study:

SR#.	TRIAL NO.	SURFACTANT NAME	SURFACTANT %
1	RF-10962	ADRENALINE ® N4950	2.0
		ADRENALINE ® N5050	2.0
2	RF-10963	ADRENALINE ® N4960	2.0
		ADRENALINE ® N5050	2.0

FORMULATION PROCEDURE FOLLOWED

Water Phase:

- Prepared the water phase by charging water, monoethylene glycol, ADRENALINE ® N5050, and antifoam.
- Mixed until a clear solution was obtained.

Oil Phase:

- Added Pyriproxyfen technical and ADRENALINE® POLYMERIC SURFACTANT in xylene.
- Mixed well until a clear solution was achieved.

Mixing Of Oil Phase Into Water Phase:

- Slowly and gradually added the oil phase into the water phase under normal stirring.

Highshear Mixing:

- Checked the viscosity of the product before initiating high shearing.
- Commenced high shearing until a D_{90} 3-5 micron oil droplet size was achieved, while maintaining the high-shear mixer operation.
- Ensured the product viscosity remained below 50cPs on spindle #63, torque 30-50% at 60RPM (Brookfield LVDV2T EXTRA; viscosity measurements may vary with different models).

Xanthan Gum Stock Solution:

- Prepared a xanthan gum stock solution in a separate vessel as per the provided formulation.

Final Adjustments:

- After achieving the required droplet size, de-aerated the trial to eliminate trapped air.
- Checked the product viscosity before adding the xanthan gum slurry.
- Added the xanthan gum stock solution to adjust the product viscosity, maintaining it at 460-480cPs on spindle #63, torque 30-50% at 60RPM (Brookfield LVDV2T EXTRA; viscosity measurements may vary with different models).

CRITICAL TO WATCH

- Viscosity after high-shearing stage should not exceed 50cPs on the given parameters
- Oil droplet size should be not greater than D_{90} 3-5 micron after high-shearing stage
- Xanthan gum stock solution should be added after proper de-aeration
- Processing temperature should be maintained between 25ºc - 30ºc

VISCOSITY & DROPLET SIZE: NORMAL MIXING OF OIL PHASE INTO WATER PHASE

TABLE 4A (Viscosity)

SR#.	TRIAL NO.	SURFACTANT NAME	SURFACTANT %	VISCOSITY AFTER NORMAL MIXING (cPs)	TEMP (ºC)	DROPLET SIZE AFTER NORMAL MIXING	
						D_{90}	D_{50}
1	RF-10962	ADRENALINE ® N4950	2.0	62	27.2	37.58	9.13
		ADRENALINE ® N5050	2.0				
2	RF-10963	ADRENALINE ® N4960	2.0	52	27	28.46	13.07
		ADRENALINE ® N5050	2.0				

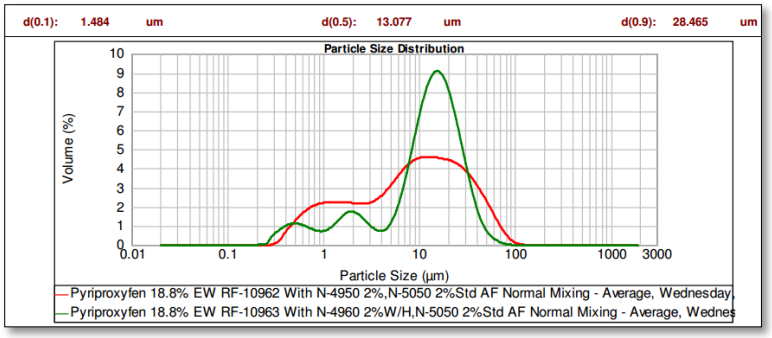
TABLE 4B (Emulsion Test (T_0) after normal mixing)

SR#.	TRIAL NO.	SURFACTANT NAME	EMULSION TIME	OIL	CREAM	SEDIMENTATION
1	RF-10962	ADRENALINE ® N4950 @2% ADRENALINE ® N5050 @2%	30min	Nil	1ml	Nil
			2hrs	Nil	2ml	Nil
			24hrs	Nil	4ml	Nil
			24.5hrs	Nil	2ml	Nil
2	RF-10963	ADRENALINE ® N4960 @2% ADRENALINE ® N5050 @2%	30min	Nil	1ml	Nil
			2hrs	Nil	3ml	Nil
			24hrs	Nil	4ml	Nil
			24.5hrs	Nil	1ml	Nil

In available trials data TABLE 4A (at normal mixing), droplet size after normal mixing and graph comparison it is established that both formulations shown almost same behavior and no abnormal change observed in both formulations. Droplet size distribution for Pyriproxyfen D_{90} varies 28micron to 37microm whereas D_{50} varies from 13micron to 9microm respectively. Whereas viscosity is around 60 cPs in both formulations.

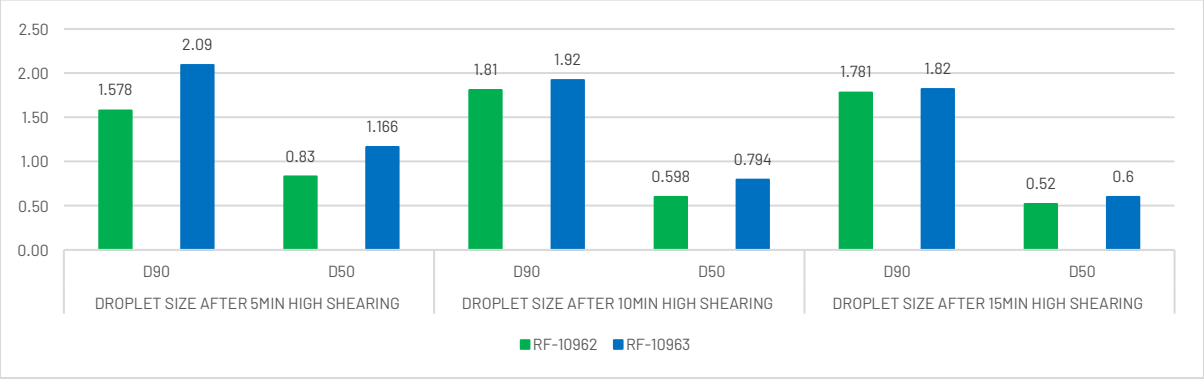
In available trials data TABLE 4B (at normal mixing), emulsion status has also almost behavior throughout the emulsion period. Both formulations have cream in 30 minutes, 2 hours, 24 hours and 24.5 hours, but no oil and no sedimentation in both trials.

Graph comparison for Pyriproxyfen droplet size at normal mixing water phase into oil phase



DROPLET SIZE STATUS AFTER 5MIN, 10MIN AND 15MIN HIGH SHEARING @ 15000RPM

GRAPHIC TABLE 5



In GRAPHIC TABLE 5, the droplet sizes after 5, 10, and 15 minutes of high shearing are presented. From the data in TABLE 5 and the graphical comparison, it is evident that after 15 minutes of high shearing, the droplet size D_{90} is less than 5 microns and D_{50} is less than 2 microns in the trial formulation RF-10962. Post high shearing, both peak patterns exhibit identical behavior, while RF-10963 shows a higher peak height than RF-10962, indicating superior droplet size reduction in RF-10963.

The desired droplet size reduction is achieved within just 5 minutes of high shearing, eliminating the need to extend the shearing time to 15 minutes. This rapid achievement of the desired droplet size and emulsion stability is a significant advantage of both formulations, ultimately reducing the overall product formulation time.

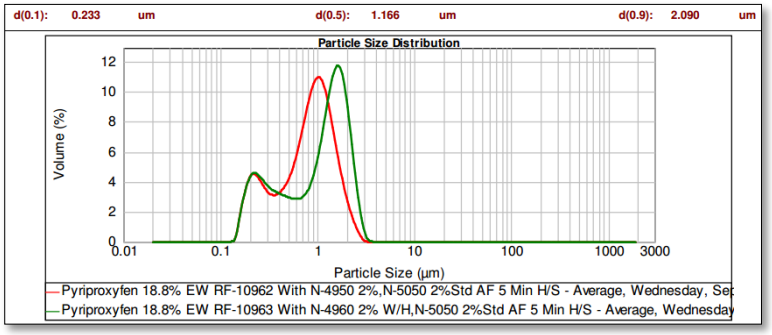
The superior performance of RF-10963, achieving a D_{90} of less than 5 microns and a D_{50} of less than 2 microns within 15 minutes of high shearing, underscores the efficacy of the ADRENALINE ® N4960 surfactant system. This rapid droplet size reduction is indicative of optimal surfactant adsorption at the oil-water interface, enhancing steric and electrostatic stabilization and preventing coalescence.

The enhanced molecular architecture of ADRENALINE ® N4960 provides improved steric stabilization and electrostatic repulsion, ensuring more efficient droplet size reduction and stability. This results in a more uniform particle size distribution, critical for the efficacy and stability of EW formulations.

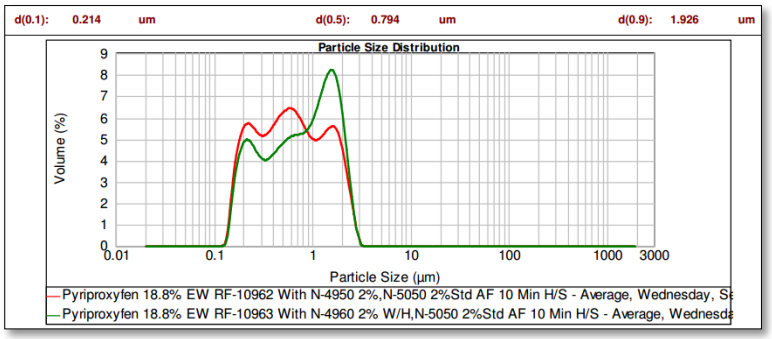
In contrast, the lack of significant droplet size reduction in RF-10962 may be attributed to insufficient surfactant concentration, suboptimal surfactant selection, or inadequate shear force application. These factors can hinder the formation of a stable emulsion, leading to larger droplet sizes and reduced emulsion stability.

The detailed analysis in subsequent tables will further elucidate the stability and performance characteristics of these formulations, providing insights into the underlying mechanisms driving these observations.

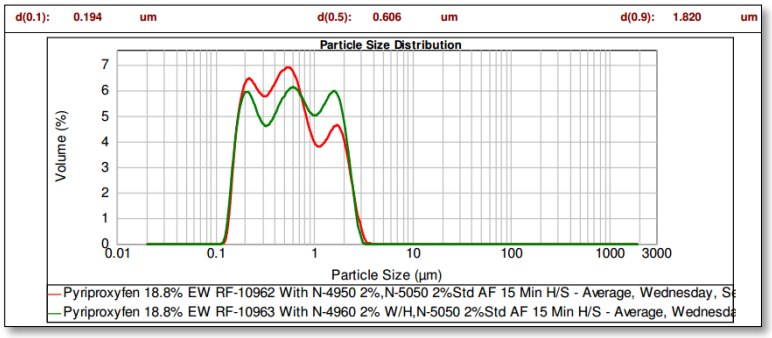
Graph comparison for Pyriproxyfen droplet size after 5min high shearing@15000RPM.



Graph comparison for Pyriproxyfen droplet size after 10min high shearing@15000RPM.



Graph comparison for Pyriproxyfen droplet size after 15min high shearing@15000RPM.



EMULSION STATUS AFTER 5MIN, 10MIN AND 15MIN HIGH SHEARING@15000RPM

Emulsion test (T_5) after 5min high shearing
TABLE 6A

SR#.	TRIAL #	SURFACTANT NAME	EMULSION TIME	OIL	CREAM	SEDIMENTATION
1	RF-10962	ADRENALINE ® N4950 @2% ADRENALINE ® N5050 @2%	30min	Nil	Nil	Nil
			2hrs	Nil	Nil	Nil
			24hrs	Nil	Nil	Nil
			24.5hrs	Nil	Nil	Nil
2	RF-10963	ADRENALINE ® N4960 @2% ADRENALINE ® N5050 @2%	30min	Nil	Nil	Nil
			2hrs	Nil	Nil	Nil
			24hrs	Nil	Nil	Nil
			24.5hrs	Nil	Nil	Nil

Emulsion test (T_{10}) after 10min high shearing
TABLE 6B

SR#.	TRIAL #	SURFACTANT NAME	EMULSION TIME	OIL	CREAM	SEDIMENTATION
1	RF-10962	ADRENALINE ® N4950 @2% ADRENALINE ® N5050 @2%	30min	Nil	Nil	Nil
			2hrs	Nil	Nil	Nil
			24hrs	Nil	Nil	Nil
			24.5hrs	Nil	Nil	Nil
2	RF-10963	ADRENALINE ® N4960 @2% ADRENALINE ® N5050 @2%	30min	Nil	Nil	Nil
			2hrs	Nil	Nil	Nil
			24hrs	Nil	Nil	Nil
			24.5hrs	Nil	Nil	Nil

Emulsion test (T_{15}) after 15min high shearing
TABLE 6B

SR#.	TRIAL #	SURFACTANT NAME	EMULSION TIME	OIL	CREAM	SEDIMENTATION
1	RF-10962	ADRENALINE ® N4950 @2% ADRENALINE ® N5050 @2%	30min	Nil	Nil	Nil
			2hrs	Nil	Nil	Nil
			24hrs	Nil	Nil	Nil
			24.5hrs	Nil	Nil	Nil
2	RF-10963	ADRENALINE ® N4960 @2% ADRENALINE ® N5050 @2%	30min	Nil	Nil	Nil
			2hrs	Nil	Nil	Nil
			24hrs	Nil	Nil	Nil
			24.5hrs	Nil	Nil	Nil

In TABLE 6a, 6b and 6c, emulsion stability at T_5, T_{10} and T_{15} of high shearing is given. Emulsion is absolutely stable throughout the high shearing process. No oil, cream and sedimentation observed in all-time series of emulsion.

%AGE YIELD AND VISCOSITY AFTER HIGH SHEARING

TABLE 7

SR#.	TRIAL NO.	SURFACTANT NAME	SURFACTANT %	YIELD %	VISCOSITY AFTER 15MIN HIGH SHEARING	
					Viscosity cPs	Temp. ^{0}C
1	RF-10962	ADRENALINE ® N4950	2.0	97.51	46	27.6
		ADRENALINE ® N5050	2.0			
3	RF-10963	ADRENALINE ® N4960	2.0	96.94	40	27
		ADRENALINE ® N5050	2.0			

Following high shear processing, two pivotal assessments—viscosity and percentage yield—are conducted to evaluate the surfactants' performance. These assessments reveal the surfactants' capacity to endure high shear forces during droplet size reduction. If the surfactant concentration and quality are suboptimal, the product's viscosity will escalate due to droplet agglomeration. This phenomenon occurs because the surfactants fail to maintain electrostatic stabilization among the droplets, which is crucial during the increase in surface area induced by high shear forces.

Table 7 demonstrates that both formulations exhibit a percentage yield around 97% and a viscosity below 50 cPs. These results indicate the precise optimization of surfactant dosage and the judicious selection of high-quality surfactants. The low viscosity reflects effective steric and electrostatic stabilization, preventing droplet coalescence and ensuring uniform dispersion. The high percentage yield underscores the surfactants' efficacy in maintaining colloidal stability and preventing phase separation under shear stress.

Viscosity after addition of slurry, final droplet size, emulsion, density@20^{0}C, pH 1% and pH5%

TABLE 8A

SR#.	TRIAL NO.	SURFACTANT NAME	SURFACTANT %	FINAL VISCOSITY AFTER ADDITION OF 3%SLURRY		FINAL DROPLET SIZE		DENSITY @20^{0}C	pH 1%	pH 5%
				Viscosity cPs	TemP. ^{0}C	D_{90}	D_{50}			
1	RF-10962	ADRENALINE ® N4950	2.0	486	29	3.00	0.59	1.023	4.6	4.12
		ADRENALINE ® N5050	2.0							
2	RF-10963	ADRENALINE ® N4960	2.0	466	28	2.01	0.68	1.031	4.73	4.31
		ADRENALINE ® N5050	2.0							

TABLE 8B

Emulsion test (T_F) after maintaining the final viscosity

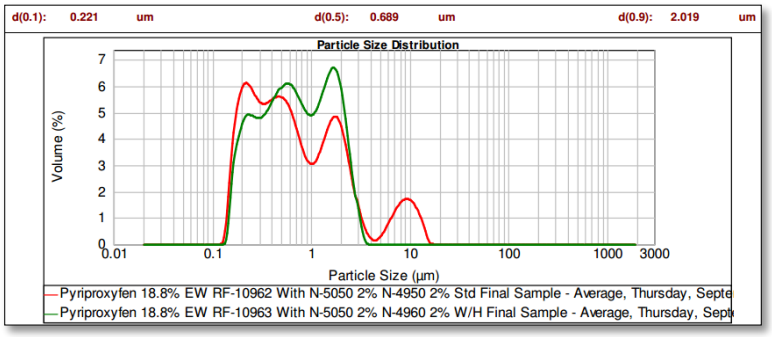
SR#.	TRIAL #	SURFACTANT NAME	EMULSION TIME	OIL	CREAM	SEDIMENTATION
1	RF-10962	ADRENALINE ® N4950 @2% ADRENALINE ® N5050 @2%	30min	Nil	Nil	Nil
			2hrs	Nil	Nil	Nil
			24hrs	Nil	Nil	Nil
			24.5hrs	Nil	Nil	Nil
2	RF-10963	ADRENALINE ® N4960 @2% ADRENALINE ® N5050 @2%	30min	Nil	Nil	Nil
			2hrs	Nil	Nil	Nil
			24hrs	Nil	Nil	Nil
			24.5hrs	Nil	Nil	Nil

TABLE 8A, expresses the analysis data after maintaining the final viscosity. All formulations have droplet size D_{90} 3-2micron and D_{50} less than 1micron respectively. Rest of time series has fit emulsion. Other test results like terminal viscosity, density, pH 1% and pH 5% are also shown in TABLE.

TABLE 8B, illustrates emulsion stability after maintenance of final viscosity, emulsion of RF-10962 and RF-10963 have 1ml and 2ml cream in 24hrs respectively, but these results are not of significance.

Graphical comparison for droplet size after maintaining the final viscosity is given below:

Graph comparison for Pyriproxyfen droplet size after final viscosity maintenance



DATA AFTER 14DAYS OF STABILITY AT 54°C

TABLE 9A

SR#.	TRIAL NO.	SURFACTANT NAME	SURFACTANT %	FINAL PS		DENSITY @20°C	pH 1%	pH 5%	PHYSICAL STATUS AFTER 14DAYS OF STABILITY AT 54°C
				D_{90}	D_{50}				
1	RF-10962	ADRENALINE ® N4950 ADRENALINE ® N5050	2.0 2.0	3.49	0.69	1.024	4.72	4.28	OK, Flowable, no Separation and no sedimentation after 14 days stability
2	RF-10963	ADRENALINE ® N4960 ADRENALINE ® N5050 @2%	2.0 2.0	1.94	0.53	1.017	4.88	4.32	OK, Flowable, no Separation and no sedimentation after 14 days stability

EMULSION TEST AFTER 14DAYS OF STABILITY AT 54°C

TABLE 9B

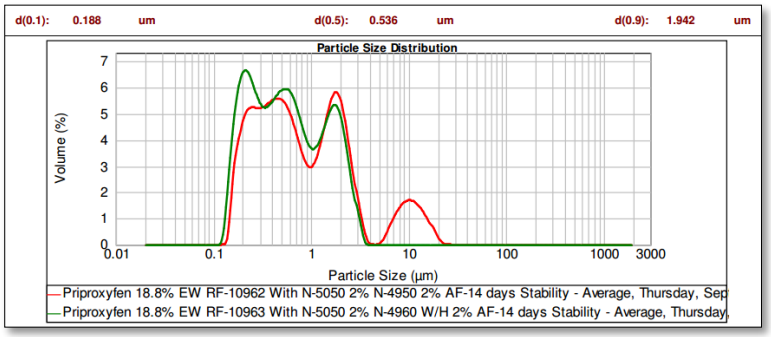
SR#.	TRIAL NO.	SURFACTANT NAME	EMULSION TIME	OIL	CREAM	SEDIMENTATION
1	RF-10962	ADRENALINE ® N4950 @2% ADRENALINE ® N5050 @2%	30min	Nil	Nil	Nil
			2hrs	Nil	Nil	Nil
			24hrs	Nil	Nil	Nil
			24.5hrs	Nil	Nil	Nil
2	RF-10963	ADRENALINE ® N4960 @2% ADRENALINE ® N5050 @2%	30min	Nil	Nil	Nil
			2hrs	Nil	Nil	Nil
			24hrs	Nil	Nil	Nil
			24.5hrs	Nil	Nil	Nil

TABLE 9A and 9B presenting the post stability data. Droplet size D_{90} and D_{50} for both trials are again at less than 5micron and 2micron respectively. Physical stability of both trials are excellent with having no separation, no sedimentation. Product is flowable and very good in smoothness.

Emulsion stability after 14days stability is also very good. Only 1ml and 2ml creaming observed in 24hrs in RF-10962 and RF-10963 respectively, but the readings at this point are of no significance.

Other test results like density, pH 1% and pH 5% are also shown in TABLE and have no significant change in pre and post stability data.

Graph comparison for Pyriproxyfen droplet size after 14days stability at 54°C.



Conclusion
Overall, the data from trials RF-10962 and RF-10963 reveal that ADRENALINE ® N4950 and ADRENALINE ® N4960 exhibit nearly identical profiles in terms of droplet size reduction during high shear processing and emulsion stability. Notably, droplet size reduction and emulsion stability are achieved in minimal time, with just 5 minutes of high shearing. All critical parameters, including droplet size reduction, viscosity during normal mixing of the oil phase into the water phase and after high shearing, emulsion stability, pH, density, percentage yield, and color before stability, show no significant deviations.

After 14 days of stability testing at 54°C, the data for droplet size, emulsion stability, pH, and density remain consistent, with no physical separation, sedimentation, or color change. The formulations remain smooth and flowable. In RF-10965, post-stability droplet size is remarkably small, with D_{90} at 3 microns and D_{50} at 0.3 microns, extending into the nanometer range. This is reflected in the sharp peak of the graphical comparison, highlighting the superior performance of ADRENALINE ® N4960 compared to RF-10964.

Droplet size reduction is a critical parameter in any EW (Emulsifiable Concentrate) formulation. Achieving a desired droplet size of less than 5 microns efficiently and effectively indicates the optimal selection of the surfactant system and its dosages. This ultimately reduces process time and enhances product stability.

Overall, no significant changes were observed during the trial formulations, with ADRENALINE ® N4950 and ADRENALINE ® N4960 performing similarly in critical parameters before and after stability testing. The enhanced molecular architecture of ADRENALINE ® N4960 provides improved steric stabilization and electrostatic repulsion, ensuring more efficient droplet size reduction and stability.

Therefore, ADRENALINE ® N4950 can be confidently replaced with the upgraded ADRENALINE ® N4960. This new formulation not only offers improved handling and a better pour point due to its lower viscosity but also ensures more efficient processing and application.

Furthermore, only 4% total surfactants are required to achieve an effective and stable formulation, which is significantly lower than in a corresponding EC (Emulsifiable Concentrate) formulation or compared to the high dosages required by monomeric surfactants in EW formulations. Additionally, the partial replacement of solvent with water offers cost benefits compared to a similar EC formulation, making ADRENALINE ® N4960 a cost-effective and high-performance solution.

FURTHER INFORMATION

Technical data sheets, safety data sheets, samples and guide formulations are available upon request. Please contact the export office or your sales contact to obtain the same.

SURFACTANT CHEMICALS COMPANY MIDDLE EAST FZC
Global Exports Division
Office C1-F1-SF0128, Ajman Freezone Building C1,
Ajman,
United Arab Emirates
Tel: +971-52-512-4789/+971-56-249-9497
Email: exportsales@surfchem.co.uk