



Crayvallac LA-100

NEW POURABLE LIQUID RHEOLOGY MODIFIER FOR POST-ADDITION TO SOLVENT-BASED COATINGS

Performance Attributes

CRAYVALLAC LA-100 is Cray Valley's first post-addition pourable liquid rheology modifier. This new product compliments our micronised product range by providing the formulator with a wider choice of incorporation techniques. CRAYVALLAC LA-100 is added to the final coating under low shear conditions where its use results in the development of an excellent shear thinning rheology characterised by very good time dependent thixotropic viscosity recovery. Consequently the primary performance advantages of using CRAYVALLAC LA-100 are:

- Excellent sedimentation suppression during storage: Under the low shear conditions that prevail during coating storage, the use of CRAYVALLAC LA-100 results in the development of a very high viscosity which effectively suppresses particle settling.
- Ease of coating application: Under the high shear conditions of coating application, this shear thinning characteristic of CRAYVALLAC LA-100 results in a low viscosity easy to apply coating.
- Good film build and levelling: Immediately following coating application the viscosity recovers in a time dependent manner. This is known as thixotropic viscosity recovery, a rheology characteristic that enables the formulator to optimise both sag control and surface levelling.

These performance attributes combine to give a well-balanced coating performance.

Activation Mechanism

CRAYVALLAC LA-100 is a low viscosity solution composed of a modified urea dissolved in N-methylpyrrolidone. When added to a coating system with the correct Solvent-balance, the modified urea separates from its carrier solvent and forms very fine fibrous crystals (See Figure 1).

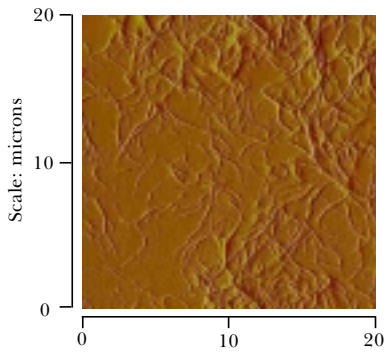


Figure 1. Atomic force micrograph of Crayvallac LA-100 in its fully activated fibrous form. Scale: Microns.

These fibres interact with each other to form a three dimensional network. It is this physical network which gives rise to the excellent shear thinning and thixotropic viscosity recovery which characterises coatings prepared using CRAYVALLAC LA-100.

Under the low shear conditions of coating storage, the modified urea fibres are essentially unrestrained and orientate themselves quite randomly. This results in a well formed fibrous network with its associated

high viscosity, and this suppresses sedimentation. The application of shear constrains this fibrous network and forces the fibres to align one with another, a condition leading to a decrease in viscosity. Under the high shear conditions of coating application a very high degree of alignment occurs. The net result of this is a very low viscosity and ease of coating application. Immediately following application, low shear conditions again prevail, and the network begins to rebuild itself in a time dependent manner as thermal energy randomises each fibre's orientation. This time dependence gives rise to thixotropic viscosity recovery, a rheological characteristic that enables the formulator to optimise both sag control and surface levelling

The general observation is that this time dependent viscosity recovery proceeds in two phases. The first occurs within a few seconds of application and results in a substantial viscosity increase, and it is this that suppresses sagging. This is followed by the second phase which has a much greater time dependence. During this time period the coating film is able to flow and attain very good surface levelling.

In order to obtain the maximum efficiency from CRAYVALLAC LA-100, it is essential to maximise the fibre forming crystallisation process. This means providing the correct Solvent-balance and efficient mixing, while at the same time avoiding the use of excessive shear which damages the crystalline fibres. Shattering of the fibres into shorter units results in a less efficient network being built.

Solvent-balance

Solvent-balance is a combined effect of the coatings binder and solvents. This concept of Solvent-balance is extremely important when using CRAYVALLAC LA-100. Coating systems with too high or too low a Solvent-balance will not provide a suitable environment for efficient fibrous crystal growth. This is easily demonstrated using xylene and n-butanol and stirring in 2% of CRAYVALLAC LA-100 in the absence of any binder:

Solvent System

n-Butanol

Complete dissolving of the liquid rheology modifier i.e. no fibres formed.

n-Butanol/Xylene 1:3

Formation of a clear solution.

Appearance of gel within 5 minutes.

Complete gelation within 10 - 20 minutes, sufficient to enable the mixture to be inverted.

Xylene

Complete separation of the rheology modifier.

Although the maximum potential is obtained from CRAYVALLAC LA-100 when the Solvent-balance has been carefully optimised, an acceptable performance may often be obtained under non-ideal conditions.

Solvent-Balance: Optimisation Procedure

In order to optimise a coating system for use with CRAYVALLAC LA-100 we propose that the following procedure be followed:

Step 1: Characterisation of the Main Solvent

Add 49 Parts of the main solvent to a glass jar. Add to this 1 Part of CRAYVALLAC LA-100. Seal the jar and shake vigorously for 5 – 10 seconds and record the immediate appearance:

Appearance

Clear solution/slight haze
Hazy
Separation and severe haze

Interpretation

This suggests the Solvent-balance may be acceptable: Go to Step 2
This is acceptable if not too extreme: Go to Step 2.
Solvent-balance unacceptable: Go to Step 2.

Leave the jar to stand and examine it at 5 minute intervals. This examination should consist of tilting the jar approximately 20 – 30° off vertical and noting any evidence of structure development e.g. thickening or appearance of gelation:

Observation

No thickening
Slight thickening
Weak gel
Strong gel

Interpretation

Further optimisation required: Go to Step 2.
Additional optimisation may be required: Go to Step 2.
Some optimising may be required: Go to Step 2.
Good Solvent-balance: Go to Step 3.

Step 2: Solvent Optimisation.

Where insufficient structure is observed in Step 1 it is necessary to modify the Solvent-balance through the addition of another solvent. Therefore it is necessary to identify acceptable secondary solvents. The procedure outlined in Step 1 is then repeated using the main solvent blended with the secondary solvent in various ratios e.g. 95:5, 90:10, 80:20 and 60:40. The following Table illustrates this process where xylene, butyl acetate and mineral spirits are the main solvents:

Solvent Ratio		Appearance	Gel Strength
Xylene	Butanol		No Structure = 1 Firm Gel = 5
80	20	Clear	5
70	30	Clear	2
50	50	Slight haze	2
Xylene	Ethylene Glycol Mono Butyl Ether		
80	20	Clear	5
70	30	Clear	2
50	50	Slight haze	1
Butyl Acetate	Butanol		
80	20	Slight haze	5
70	30	Slight haze	4
50	50	Slight haze	2
Butyl Acetate	Iso-Butanol		
80	20	Slight Haze	4
70	30	Slight haze	5
50	50	Slight haze	5
Mineral Spirits	Iso-Butanol		
80	20	Very hazy/some separation	1
70	30	Very hazy	2
50	50	Hazy	4

From this screening exercise we find that several solvent combinations result in good structure development.

Step 3: Optimisation of the Binder and Solvent Combination.

At Step 2 the choice of secondary solvent is decided and an approximation is made as to a suitable blending ratio. It is now important to further define the blending ratio in the presence of the binder. In general the binder is another source of the main solvent and care must be taken to allow for this in the Solvent-balance. To a jar is added 49 Parts total of the binder, main solvent and sufficient secondary solvent to give the required solvent blend ratio. This mixture is vigorously agitated to ensure homogeneity. To this is then added 1 Part CRAYVALLAC LA-100 and the mixture again agitated to ensure homogeneity. Depending on the viscosity of the system, shaking may be insufficient. In this case we recommend controlled mechanical stirring to achieve homogeneity. When mixing is complete the appearance should be immediately noted and the structure examined over a period of several hours. The quality of structure at this stage could be made visually or by the use of test equipment such as viscometers or gel-strength testers.

Observation

Clear solution with a good level of structure.

Slight haze with a good level of structure.

Very hazy with minimal structure.

Interpretation

Good Solvent-balance.

Good Solvent-balance.

Solvent-balance questionable.

Note: In some systems the fibre forming process may take several hours for complete development.

Where the Solvent-balance is judged to be insufficient Step 3 should be repeated with minor adjustments being made to the concentration of secondary solvent.

Step 4: Paint Testing

The final test is to confirm the paint performance for the chosen solvent blend. As to whether the system is acceptable, or not, is a judgement based on many parameters for the formulator e.g. anti-settle performance, sag resistance, in-can appearance, storage stability, ease of application etc. Small adjustments to the secondary solvent concentration at this stage may also prove beneficial with additional performance gains being made. The initial structure development may take several hours with the equilibrium result requiring a couple of days.

To the final paint formulation with the correct Solvent-balance is slowly added the CRAYVALLAC LA-100 under conditions of good agitation. Excessive shear should be avoided as this may result in poor structure development. The coating is then left to stand for several hours and the structure development is monitored with time.

In order to achieve a high degree of reproducibility with coating formulations it is worth noting the following:

- The addition procedure for CRAYVALLAC LA-100 should be standardised.
- It is important to ensure that CRAYVALLAC LA-100 is added under conditions that facilitate homogeneity e.g. efficient mixing without excessive shear.
- CRAYVALLAC LA-100 should be added as a slow stream to facilitate efficient dispersion.

Solvent-Balance Optimisation: Xylene Based Industrial Alkyd.

The following outlines the optimisation of a short oil alkyd topcoat based on SYNOLAC 27X from Cray Valley. For this topcoat it is estimated that a binder to solvent ratio of 48:30 will be required. This means that for every 48 Parts of SYNOLAC 27X added an additional 30 Parts of solvent will be required:

Step 1: Characterisation of the Main Solvent

Test Results: Main Solvent - Xylene

Immediate Appearance	Hazy with complete separation.
Structure Development	No structure development after one hour
Conclusion	Poor solvent-balance: Go to Step 2.

Step 2: Solvent Optimisation using Ethylene Glycol Mono Butyl Ether (BGE).

Test Results: Xylene/BGE 95:5

Immediate Appearance	Very hazy with separation.
Structure Development	Slight structure development.
Conclusion	Unacceptable Solvent-balance.

Test Results: Xylene/BGE 90:10

Immediate Appearance	Slight haze.
Structure Development	Gel formed within 45 minutes.
Conclusion	Borderline acceptability

Test Results: Xylene/BGE 80:20

Immediate Appearance	Clear.
Structure Development	Firm gel within 45 minutes.
Conclusion	This solvent ratio will most likely provide an acceptable Solvent-balance for CRAYVALLAC LA-100 in the final coating: Go to Step 3.

Test Results: Xylene/BGE 70:30

Immediate Appearance	Clear
Structure Development	Firm gel within 45 minutes.
Conclusion	Good Solvent-balance but BGE level considered too high.

Step 3: Optimisation of the Binder and Solvent Combination.

This optimisation process is based on the anticipated ratio for SYNOLAC 27X to additional solvent being 48:30 in the final coating. From Step 2 it was identified that an 80:20 blend of xylene and BGE will most likely provide an acceptable Solvent-balance for CRAYVALLAC LA-100. Therefore it will be necessary to combine 48 Parts of SYNOLAC 27X with 30 Parts of xylene/BGE (50:50) to ensure that the final mixture has a solvent ratio of 80:20 with respect to the total xylene and BGE concentrations. Due to the thickening effect of the binder it was necessary to use mechanical stirring. To this mixture was added 2% of CRAYVALLAC LA-100 under stirred conditions.

Test Results: SYNOLAC 27X/Xylene/BGE

Immediate Appearance	Clear initially.
Structure Development	Became hazy and structured to an acceptable level within one hour.
Conclusion	Proceed to Step 4.

Step 4: Paint Testing.

Based on the results and conclusions from Steps 1 - 3, the following topcoat was prepared by thinning with xylene/BGE (50:50) such that a final xylene to BGE solvent ratio of 80:20 is obtained prior to the addition of CRAYVALLAC LA-100:

Components	Parts (w/w)	Process
Millbase		
Rutile Titanium Dioxide	238.8	The millbase was prepared using a high-speed disperser operating under optimum dispersion conditions.
SYNOLAC 27X	112.8	
Xylene	10.0	
Letdown		
SYNOLAC 27X	465.5	To the millbase was added the binder, driers, and MEKO. The mixture was then thinned using the xylene/BGE (50:50) to a final viscosity of 300 mPa.s (ICI Cone and Plate: 10000s ⁻¹). To this mixture was added the CRAYVALLAC LA-100 as a slow stream under low shear conditions (High-speed disperser: Peripheral speed = 2.5 ms ⁻¹).
Driers (Co:Zr:Zn)	9.7	
MEKO	1.2	
Xylene/BGE 50:50	150.0	
CRAYVALLAC LA-100	12.0	
	1000.0	

The following results were obtained for this coating when tested 24 hours later:

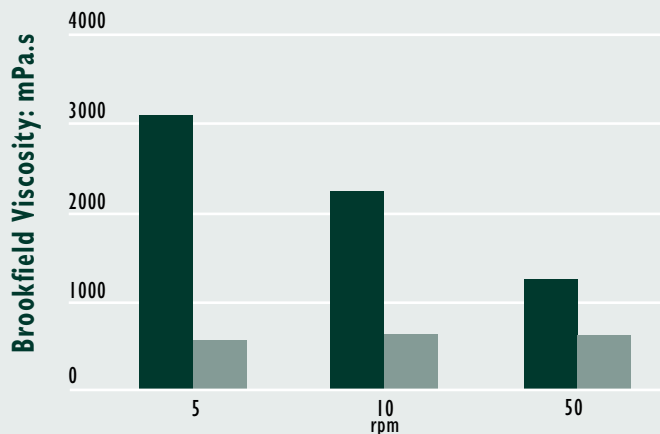


Figure 2: Brookfield viscosity data for a SYNOLAC 27X industrial alkyd topcoat modified with CRAYVALLAC LA-100. All results were measured using spindle 3 at 23°C (73°F). **Light Green:**Control, no rheology modifier added. **Green:**1.2% CRAYVALLAC LA-100 added.

Sag measurements indicate a maximum wet film thickness of 125 microns for the control and 250 microns when modified with CRAYVALLAC LA-100. These results demonstrate the potential of CRAYVALLAC LA-100 to address anti-settle and sag issues. Although these initial results were considered sufficient, fine tuning of the secondary solvent and CRAYVALLAC LA-100 concentrations would normally be done in order to fully optimise the performance. This would involve making small increases and decreases to both concentrations in an ordered manner e.g. statistical experimental design.

Solvent-Balance Optimisation: Solvent-Based Epoxy Topcoat.

The following outlines the optimisation of a conventional solvent based epoxy topcoat based on Epikote 1001-X70 and Cray Valley's CRAYAMID 195X polyamide based curing agent:

Step 1: Characterisation of the Main Solvent

Test Results: Main Solvent - Xylene

Immediate Appearance	Hazy with complete separation.
Structure Development	No structure development after one hour
Conclusion Incompatible:	Go to Step 2.

Step 2: Solvent Optimisation using n-Butanol.

Test Results: Xylene/Butanol 85:15

Immediate Appearance	Clear.
Structure Development	Soft gel within 20 minutes.
Conclusion	Insufficient structure.

Test Results: Xylene/Butanol 75:25

Immediate Appearance	Clear.
Structure Development	Formation of a firm gel within 15 minutes.
Conclusion	This solvent ratio will most likely provide an acceptable Solvent-balance for CRAYVALLAC LA-100 in the final coating. Go to Step 3.

Test Results: Xylene/Butanol 65:35

Immediate Appearance	Clear.
Structure Development	Slight structure development after 1 hour.
Conclusion	For technical reasons, the level of butanol was considered too high.

Step 3: Optimisation of the Binder and Solvent Combination.

Due to the thickening effect of the binder it was necessary to use mechanical stirring when incorporating the CRAYVALLAC LA-100. The Epikote 1001-X70 was diluted to give a final xylene/butanol ratio of 75:25 and a realistic epoxy concentration

Test Results: Epikote 1001-X70/Xylene/Butanol

Immediate Appearance	Clear initially.
Structure Development	High level of structure formed within 1 hour.
Conclusion	Proceed to Step 4.

Step 4: Paint Testing.

Based on the results and conclusions from Steps 1 - 3, the following epoxy topcoat was prepared. Both the epoxy component and the final formulation containing the polyamide curing agent were formulated so that the xylene/butanol ratio remained constant at 75:25.

Components	Parts (w/w)	Process
Part A: Millbase		
Rutile Titanium Dioxide	278.5	The millbase was prepared using a high-speed disperser operating under optimum dispersion conditions.
Epikote 1001-X75	92.5	
Xylene	10.0	
n-Butanol	10.0	
Part A: Letdown		
Epikote 1001-X75	207.2	To the millbase was added the binder. The system was then thinned with xylene and butanol to a final viscosity of 400 mPa.s (ICI Cone and Plate: 10000s ⁻¹) with a final xylene/ butanol ratio of 75:25. To this mixture was added the CRAYVALLAC LA-100 as a slow stream under low shear conditions (High-speed disperser: Peripheral speed = 2.5 ms ⁻¹). This epoxy component was then left for 24 hours before combining with the curing agent.
Xylene	64.9	
n-Butanol	40.2	
CRAYVALLAC LA-100	14.0	
Part B: Curing Agent		
CRAYAMID 195X	200.7	To the above epoxy component was added the CRAYAMID 195X and the mixture thinned to 400 mPa.s (ICI Cone and Plate: 10000s ⁻¹) with xylene and butanol to give a final solvent ratio of 75:25.
Xylene	61.5	
Butanol	20.5	
	1000.0	

The following test results were obtained:

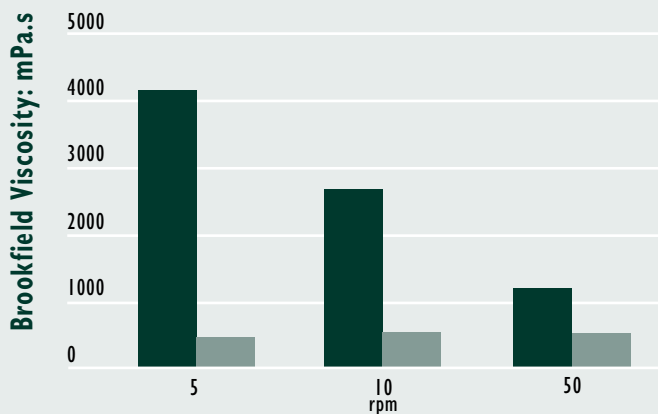


Figure 3: Brookfield viscosity data for a solvent based epoxy topcoat modified with CRAYVALLAC LA-100. All results were measured using spindle 3 at 23°C (73°F). **Light Green:**Control, no rheology modifier added. **Green:**1.4% CRAYVALLAC LA-100 added.

Sag measurements indicate a maximum wet film thickness of 125 microns for the control and 425 microns when modified with CRAYVALLAC LA-100. These results clearly demonstrate the potential of CRAYVALLAC LA-100 to address anti-settle and sag issues.

Precautions

CRAYVALLAC LA-100 is sensitive to moisture due to the hygroscopic nature of N-methylpyrrolidone. Therefore all containers must be tightly sealed after use to prolong storage stability. The absorption of water from the atmosphere will result in the premature crystallisation of the modified urea.

This information is given to the best of our knowledge. However, due to the multitude of formulations, processing methods and application conditions used in the field, we strongly recommend that all products containing CRAYVALLAC LA-100 be tested thoroughly to ensure suitability for their intended end use. In particular, application in poorly ventilated areas, or on hot substrates, or by hot spray, may require additional attention.

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