



Hydrogenated Castor Oil Based Rheology Modifiers

Shear thinning and thixotropic viscosity recovery

The need to modify the viscous properties of a solvent-based coating is universal with respect to three major considerations:

- **Sedimentation:** During storage, the coating must develop a very high viscosity in order to effectively suppress settling of pigments and extenders.
- **Coating Application:** The coating viscosity must be sufficiently low for ease of application by conventional methods e.g. brush, roller and spray.
- **Levelling:** Once applied, the coating must exhibit the correct rheological characteristic so that sag resistance is maximised without detriment to the surface levelling process.

In order to satisfy the first two conditions, suppression of sedimentation and ease of application, the coating system must adopt what is known as shear thinning rheology. This is characterised by a very high viscosity under low shear conditions, such as those experienced by a coating during storage, and a low viscosity under the high shear conditions of application.

Immediately following application, the coating film is now subjected to the low shear conditions of gravity. Here it is desirable that the film remains in place during the drying process and also that a high degree of surface levelling be obtained. In order to effectively address sag resistance and surface levelling at the same time, the coating system must exhibit a time dependent viscosity recovery, a process known as thixotropic recovery. This is where the viscosity of the coating film increases in a time dependent manner back towards its low shear value. The increase in viscosity suppresses sagging while the time dependent aspect allows sufficient time for effective levelling. If this time dependent viscosity recovery is too rapid, the coating will essentially behave in a pseudoplastic manner. While this will result in excellent sag resistance, the result will be poor surface levelling with any application textures such as brush marks permanently frozen in as a feature of the dried film. Consequently, shear thinning rheology combined with time dependent thixotropic viscosity recovery is a feature highly sought after for most coatings.

There is a wide range of rheology modifiers available to the formulator e.g. silicas, organo-clays, organo-waxes, polyethylene waxes and various surfactants. Unfortunately, most of these exhibit very little time dependence following application i.e. they tend more towards a pseudoplastic rather than the well balanced thixotropic rheology.

Hydrogenated castor oil based rheology modifiers are one particular group of rheology modifiers that impart an excellent thixotropic character to solvent-based coatings. The general performance characteristics of these are:

- Ease of incorporation.
- Excellent suppression of sedimentation.
- Very good shear thinning characteristics during application.
- Very good sag resistance and surface levelling.

These properties combine to give a coating system an optimum combination of in-can appearance, sedimentation suppression, ease of application, sag resistance and film levelling.

Hydrogenated Castor Oil Based Rheology Modifiers

Cray Valley has three different grades of hydrogenated castor oil based rheology modifiers:

Antisettle CVP Flowtone R Flowtone GR	Hydrogenated castor oil.
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Crayvallac MT Flowtone ST Flowtone GST	Amide modified hydrogenated castor oil.
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Crayvallac SF Crayvallac SF2	Speciality amide modified hydrogenated castor oil.
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Table 1: Cray Valley's range of hydrogenated castor oil based rheology modifiers. FLOWTONE GR is a 50/50 blend of hydrogenated castor oil and kaolin. FLOWTONE GST is a 50/50 blend of amide modified hydrogenated castor oil and kaolin. CRAYVALLAC SF2 is the marketing name used for CRAYVALLAC SF in North America.

All three grades are recommended for general use in surface coating formulations to promote the following properties:

- Pigment suspension.
- Ease of application.
- Good brushability.
- Very good sag resistance on vertical surfaces.
- Edge cover.
- Film build.
- Hold out over porous substrates.
- In-can consistency.

Where these products differ is in their tolerance towards solvent strength and processing temperature.

Product Selection Guide

The following table illustrates the suitability of each product in relation to different solvent types and processing temperatures:

	Antisettle CVP Flowtone R Flowtone GR	Crayvallac MT Flowtone ST Flowtone GST	Crayvallac SF Crayvallac SF2
Mineral Spirits	30 – 55°C (86 - 131°F)	35 – 75°C (95 - 167°F)	Not recommended
Aromatic Hydrocarbons	Not recommended	30 – 50°C (86 - 122°F)	30 – 65°C (86 - 131°F)
Aromatic Hydrocarbon and Alcohol Blends	Not recommended	30 – 50°C (86 - 167°F)	30 – 65°C (86 - 131°F)
Aromatic Hydrocarbon and Glycol Ether Blends	Not recommended	< 50°C (122°F)	< 65°C (149°F)

Note: The information given above is provided as a basic guideline for product selection. However, due to the numerous variations in resin type, storage conditions and application methods used in the field this selection table should not be taken as a guarantee of product suitability.

Table 2: Guidelines for matching Cray Valley's hydrogenated castor oil based products to various coating systems and processing temperatures.

Incorporation and Activation Techniques

Hydrogenated castor oil based rheology modifiers may generally be incorporated and activated by the use of the following equipment:

- High-speed dispersers.
- Bead mills and attritors.
- Ball mills.
- Triple roll mills.

Where sufficient dispersion time is not always possible, it is often beneficial to replace the rheology modifier with its kaolin based version e.g. substitute FLOWTONE R with FLOWTONE GR, and FLOWTONE ST with FLOWTONE GST. These kaolin grades are characterised by much faster dispersion and activation times.

The following guidelines are given to assist in the design of a suitable incorporation and activation process for Cray Valley's range of hydrogenated castor oil based rheology modifiers.

High-Speed Dispersers:

These are ideal in that they readily develop the necessary shear and temperature conditions for complete activation. The rheology modifier is generally added to the high-speed disperser along with the initial charge of solvent and binder followed by the pigments and extenders. The high-speed disperser is then set to operate at its optimum dispersion condition. The dwell-time under dispersion conditions should preferably be in the order of 20 - 30 minutes and within the recommended temperature ranges to ensure full activation and dispersion. During this process the temperature rise is rapid and care should be taken not to exceed the maximum indicated. If the temperature should rise above the recommended maximum it may be necessary to cool the paint to below the minimum activation temperature under continuous low speed stirring to prevent seeding and to obtain a satisfactory result.

Ball Mills:

Hydrogenated castor oil based products can be charged into the mill with the normal mill charge. The temperature developed in these mills is usually adequate for optimum dispersion although control of the temperature is sometimes difficult. If an excessive temperature is generated this could result in seeding due to the very long processing times involved.

Bead Mills and Attritors:

This type of continuous dispersion equipment needs special attention because the residence time in the mill is very short. The generation of too high a temperature must also be avoided as this will result in partial dissolving of the hydrogenated castor oil fraction. Generally the residence time of the coating within the dispersion zone is too brief (e.g. 1 - 10 minutes) to ensure complete activation. This may result in the finished coating containing very fine particles of inactive rheology modifier which later swell on storage to give a seedy or bitty texture. Two precautions may be taken to avoid this problem, either the rheology modifier can be added to the dispersion charge as a pregel in solvent or the charge can be premixed thoroughly on a high-speed disperser before passing through the mill. In either case, the process should be studied carefully to ensure that the milling results in complete activation of the rheology modifier.

Triple-roll Mills:

With these mills, the temperature development and residence time will be minimal. Consequently their use is not ideally suited for the direct incorporation of these rheology modifiers. Here a pregel technique is recommended as well as ensuring that the dispersion on the mill achieves full activation temperatures for at least a 20 minute dwell-time. Certainly some predispersion of the mill base will be advantageous and heating through the rollers will also be beneficial.

Pregel Techniques

The pregel technique involves the preparation of a premix of the rheology modifier at a high concentration in a solvent or a low solids solution of the binder. This results in the formation of a deagglomerated, presoftened and preswelled paste. The paste is then high shear dispersed at an elevated temperature in order to obtain full activation. This technique is recommended for any incorporation process where dwell-time is inadequate.

For the pregel preparation a conventional high-speed disperser can be used or preferentially a kinetic mixer (high-speed stator/rotor disperser). In preparing a pregel we recommend high-speed stirring at a final additive concentration of about 15%. It may be beneficial for the initial concentration of the pregel to be high (e.g. 30% solids) so that the early consistency will be increased. This allows the development of better shear and improved temperature increase in the relatively low viscosity mixture. More solvent should be added as the paste begins to thicken. A final pregel solids content above 15% will result in a very strong paste which will be difficult to handle. During this process it is essential that the temperature be allowed to rise above the minimum suggested for the particular solvent combination. Gelation of the charge occurs soon after the temperature is reached.

Typically the process time will be 15-30 minutes depending on the scale of the pregel and the power input of the stirrer. The pregel will develop its full structure after standing overnight and will remain stable if stored under normal ambient temperature conditions. The storage containers should be sealed to prevent solvent loss and drying of the pregel surface. These pregels must be incorporated at the dispersion stage and are not suitable for post-addition.

Incorporation and Activation Precautions

Insufficient dispersion and grinding will result in a final coating which contains very fine particles of inactive rheology modifier. Although these will not show up on the grind gauge at the time of manufacture, they will slowly swell in size during storage to produce a bitty coating. This aspect is more of a problem when preparing coatings containing very weak solvents e.g. mineral spirits and deaerated mineral spirits. Recovery of these paints will require redispersion as outlined on the next page for paints in which the hydrogenated castor has solubilised during manufacture.

Excessive processing and the exposure of hydrogenated castor oil based products to too high a temperature during coating manufacture may cause partial or even total solubilisation. These products are especially sensitive to such misuse. When solubilisation occurs, it often leads to uncontrolled recrystallisation of the hydrogenated castor oil fraction during cooling. This will result in a final coating with a bitty or seedy appearance. Should this occur then recovery of the coating may be possible by following one of the following procedures:

- Reheat the seedy or bitty coating to its appropriate activation temperature and stir until the desired coating appearance is obtained. With continuous stirring, cool the coating back to ambient.
- If the coating viscosity is sufficiently high, the seedy or bitty aspect may be removed by regrinding with a high-speed disperser.
- If the coating viscosity is too low, regrinding to remove the seedy or bitty nature will require the use of a bead or ball mill.

Stability and Seed Resistance

Coatings prepared using hydrogenated castor oil based thixotropic modifiers rarely exhibit satisfactory resistance during prolonged exposure to temperatures in excess of 40 – 50°C. Instability manifests itself in the form of a downward viscosity drift or the appearance of seedy bitty particles. Seeding is often the reason for a decrease in gloss during storage. The recovery of degraded paints may often be achieved by following the guidelines outlined in the previous section.

False-Body

As with all rheology modifiers based on hydrogenated castor oil, coatings may sometimes develop an excessively high structure, or false-body. This results when the hot coating is allowed to cool in the absence of stirring. This effect is minimised by cooling the coating with stirring to less than 40°C prior to discharge. Fortunately, this false-body phenomenon is a temporary effect and can be removed by the application of shear.

The presence of false-body in a coating manifests itself as a higher than normal viscosity. The consequence of this misinterpretation during manufacture generally results in the addition of excess solvent with the result of an over-thinned coating being produced. Due to the potential for false-body to occur, care must therefore be taken to ensure that process and quality control tests are not carried out on affected samples. This is best achieved by pre-conditioning all samples by mechanical stirring for several minutes prior to testing.

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