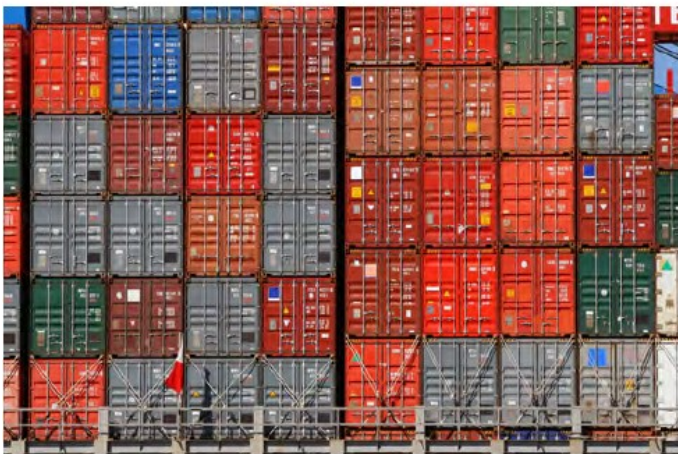


THIXCIN[®] and THIXATROL[®]

Background, mechanism and activation from the first generation of castor waxes to modern diamide based grades



Introduction

Organic thixotropes have been developed to provide outstandingly high sag and slump control in non-aqueous systems such as paints, coatings, adhesives or sealants. Due to their unique performance range, organic thixotropes are strongly differing from other rheology modifiers.

Organic thixotropes out of the THIXATROL® and THIXCIN® product family are based either on ricinus oil derivatives, also called castor wax, or diamide waxes.

The main benefits of this class of rheology modifiers are the following:

- Shear thinning flow with very high thixotropy
- Outstandingly high yield values
- Optimum sag and slump control
- Very high film build
- Stable suspension of pigments and extenders
- Excellent control of syneresis and separation
- Give stable package viscosity

All described classes of organic thixotropes can be formulated in solvent based or solvent free systems and are providing unique properties. However, a specific activation process which includes high shear and elevated temperature has to be respected to achieve the performance. In addition, the activation process is highly system dependent and will change as soon as raw material modifications in the final systems are relevant.

The advantages and limitations of this product class will be explained and discussed in the following article. Further, an overview on available products within the portfolio with detailed explanations regarding the necessary application processes from the first generation of castor waxes to the last generation of diamide waxes will be given. This latest addition to the portfolio offers the best ratio between incorporation

Class comparison

Organic rheological additives based on castor wax and diamides provide outstandingly high low shear viscosity in combination with a strong thixotropic flow character in non-aqueous systems. As described in *figure 1*, the hysteresis area, which is an important indicator for the mentioned thixotropy, is much larger with organic thixotropes in comparison to organoclays. Polyethylene based anti-settling additive are only active at ultra-low shear rates.

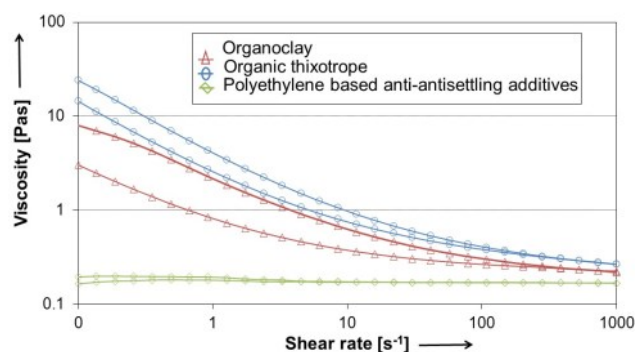


Figure 1: Comparison thickener classes

The graph displays that organic thixotropes are providing the highest film build properties. Organoclays are acting more beneficial in terms of levelling combined with well-balanced anti sag performance. Polyethylene based grades are only providing anti-sedimentation stability.

Chemical background

The first generation of organic thixotropes has been based on castor oil gained from the castor bean which is primarily grown in India. Its oil is a fatty acid triglyceride and contains large amounts of ricinoleic acid, chemically an unsaturated 12-hydroxy octadecenoic acid. As visualized in *figure 2*, a hydrogenisation eliminates the majority of the unsaturated groups to create a solid castor wax named trihydroxystearin.

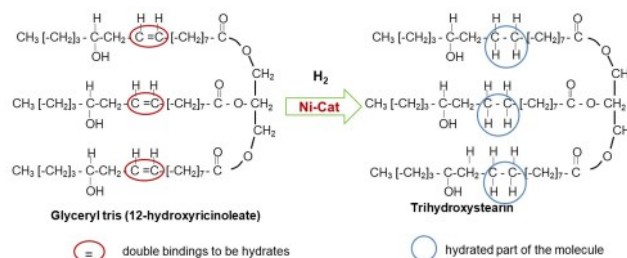


Figure 2: Hydrogenation process of castor oil

Hydrogenated castor oil works well as a rheological additive providing excellent performance when incorporated in a specific manner. Before being usable as such, the material must undergo further processing steps such as a micronisation step.

Pure castor waxes are typically limited in use for aliphatic solvent based- and solvent-free systems. To generate a rheology modifier suitable for solvents of higher polarity, such as aromatics, it is necessary to shift the melting point of the castor wax upwards by the addition of higher melting components. This broadens the range of compatible solvents, but the general activation temperature will rise in comparison to pure castor waxes. None of the ricinus oil derivatives are suitable for systems formulated with solvents of high polarity, such as oxygenated solvents e.g. ketones and esters.

Once properly activated, castor waxes are increasing the viscosity, structure and yield points of the formulated systems by associations with solvents and polymer forming bridging micelles.

The second class of rheology modifiers for the mentioned spectrum of application is based on diamide waxes which is consisting of a different, in *figure 3* described general molecule structure.

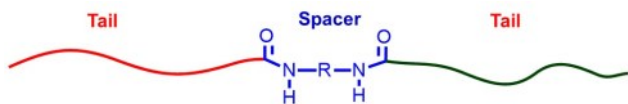


Figure 3: Diamide molecule schema

Due to the nature of the amide functionality, once properly activated, the molecules are orienting themselves to each other forming a fibrillar structure. The driving force for this formation are intermolecular interactions such as hydrogen bonding, van-der-Waals forces, etc.

The in *figure 4* visualized intermolecular interactions are becoming relevant after activation of the additive which is similar to them of castor waxes. For proper activation, also mechanical forces at the correct temperature, which has to be in line with the relevant solvency forces, in the system need to be applied. The rheological structure is then build up by a redistribution of crystalline phases of rheological additive accompanied by cooperative self-assembly of certain molecules producing the described microstructure.

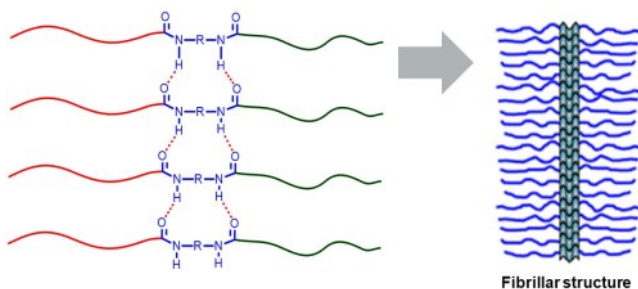


Figure 4: Molecular orientation diamide

The melting point of the diamide is tendentially higher than those of castor oil derivatives. This on one hand enables this class of rheology modifiers for the use in the largest range of solvent based systems. On the other the potential activation temperatures are tendentially higher than with castor wax based grades.

Activation process

Historically, diamide and castor wax based rheology modifiers were developed for solvent borne applications in which a high amount of rheological structure was needed. The selection of a suitable organic thixotrope, which is shown in *table 1*, has to be done in accordance with the polarity of the solvents

used and the ability to control the processing temperature.

Product	Solvent free systems		Solvent system	
	Aliphatic		Aromatic	Oxygenated
Ricinus derivatives				
Castor wax	60-70	35-50	not recom.	not recom.
Polyamide modified castor wax	80-90	55-75	30-50	not recom.
Diamide waxes				
Conventional diamide	85-100	60-75	45-60	35-45

Table 2: Recommended processing temperature

As the elevated temperature in processing of organic thixotropes can be seen as an equivalent to the solvency of a system, the higher the solvency the lower the required processing temperature will be. Tendentially, oxygenated solvents, such as ketones and esters, have got the highest polarity and are therefore providing the highest solvency. On the other hand, aliphatic solvents is having the lowest solvency and require therefore higher activation temperature. This consequently means, that in case of solvent free systems, and high-solids where solvency forces are on the low side, the potential activation temperature is always on the high side.

Castor wax based additives are normally good products for solvent based systems of low to medium polarities, such as aromatics and aliphatics as well as for solvent free systems. For higher polar solvents, e.g. ketones and esters, castor waxes are not suitable due to too low activation temperatures which can sometimes be equal or below to the room temperature. However, in case of solvent free systems the needed activation temperature is often in a moderate range which is typically seen as a large benefit.

Beside the solvent range covered by ricinus oil derivatives, diamide based organic thixotropes are suitable for systems containing solvents of higher polarity at quite moderate temperatures. On the other hand, in case of solvent free systems as well as application containing solvents of low and medium polarity, the activation temperature with diamides can be sometimes quite high. This fact is often not wanted, as most of the producers are using just the heat generated by the friction during dispersion. From this point of view, the recently introduced new class of diamides acts much more beneficial.

The activation process of organic thixotropes itself, which are being supplied as dry powder, has to follow a strict procedure and order of addition to achieve the optimum activity. These procedure, described in *figure 6*, is especially related to high shear, elevated temperature and dwell time.

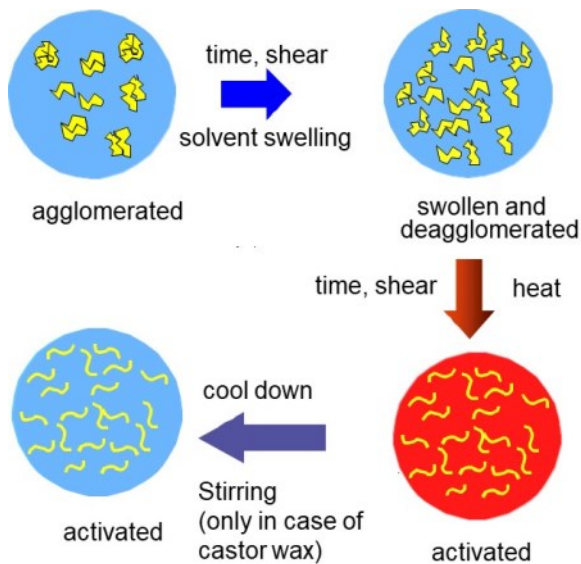


Figure 5: Activation process

All these additives need to be subjected to solvent wetting, deagglomeration and high shear forces at a specific temperatures which is depending on the system. In an ideal case, the organic additive is being exposed to the binder resin or a solvent/resin blend and homogenized using moderate shear for approximately 5 minutes. Afterwards other raw materials, e.g. pigments/extenders and other additives e.g. surfactants, can be added under agitation. In the following dispersion step, high shear at the recommended temperature need to be applied for at least 15-30 minutes before the letdown is initiated. In case of castor waxes, the cool down process should be done under moderate shear until an ambient temperature is reached to avoid so called “false body” effects”.

As mentioned, the choice of the correct activation temperature range in elementary and should be done carefully. The general temperature range can be read out of *table 1*. However, in certain case, e.g. when solvents blends are used, the preselection of the correct activation temperature can be quite complex. As visualized in *figure 6*, in this cases it is recommended to perform a ladder study with the organic thixotrope in the relevant system.

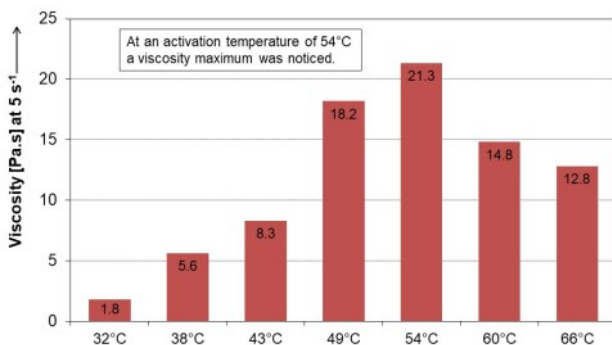


Figure 6: Temperature ladder study

In such ladder study, in this case a pure castor wax in an alkyd based varnish, several batches of the relevant systems have to be prepared with identical concentrations of rheology modifier. Only the activation is done using individually different temperatures. All other parameter, e.g. shear and dwell time, are kept constant. The optimum temperature can be identified at a viscosity maximum after the final preparation and cool down to a specified temperature. With furtherly enhancing temperatures sometimes a viscosity decrease is noted. This is quite often the case with castor wax based additives due to seeding effects. However, also the activation time at the relevant temperature is very important.

It can be seen in *figure 7*, that from the optimum activation temperature a further viscosity increase can be achieved with an elongation of the activation period. However, from a certain maximum activation time no further improvement can be obtained with additional time. The shown example was with a diamide modified castor wax taken in an aromatic free alkyd resin.

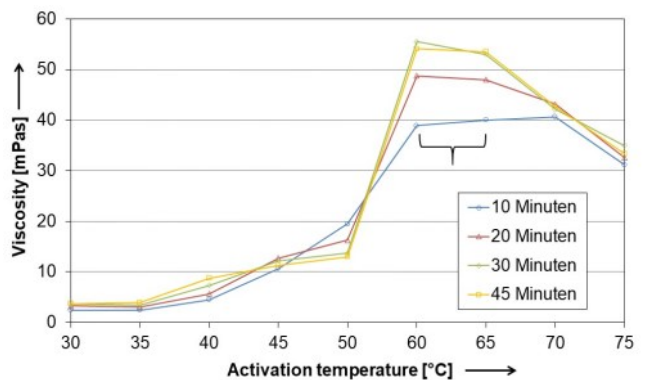


Figure 7: Time dependency activation

Due to the described complexity of the handling and activation of castor wax and conventional diamide based organic thixotropes, the initially mentioned new class of diamide rheology modifiers has been developed to be applicable at markedly lower temperatures than traditional grades based on similar chemistry. This is rather important in solvent-free systems where tendentially the activation time is on the high side. The main advantage of such low temperature activation is the limitation of the entire processing temperature of the relevant end system which results in a significant cost benefit for the manufacturer.

Another major focus of the development was, to generate organic thixotropes which are acting mostly independent from potential temperature variations in processing to provide stable viscosity build over a wider temperature range. This results in increased process robustness under real life conditions.

Side effects

In case the activation conditions chosen for the activation of organic thixotropes are not ideally in line with the composition of the relevant application, certain side effects might occur. These side effects are either so called “seeding” and the appearance of “false bodies”. It is generally much more likely to experience these side effects with the use of castor wax derivatives, as both effects are strongly related to the melting point of the additives. One exception is “latent seeding” which might also occur with the use of diamides.

Due to the significantly higher melting point of the diamide grades in comparison to castor waxes is significantly higher, the risk of classic seeding and false body effects are limited to a minimum. Note, the risk of false body and classic seeding effects is not eliminated with the use of diamides. It is shifted into a temperature range which is typically not reached in paint and coating production.

As already described, the activation conditions with respect to high shear, choice of the correct activation temperature and dwell time must be met for successful processing. When selected, correctly for the relevant system, the additives are not being put into a real solution, but rather being processed into a colloidal stage. In such colloidal stage the products are able to form the bridging micelles providing the observed viscosity increase.

As it can be seen in *figure 8*, in case the processing temperature was set too high, or applied for too long, the polymer will partially or totally solubilize during the heated portion of the process.

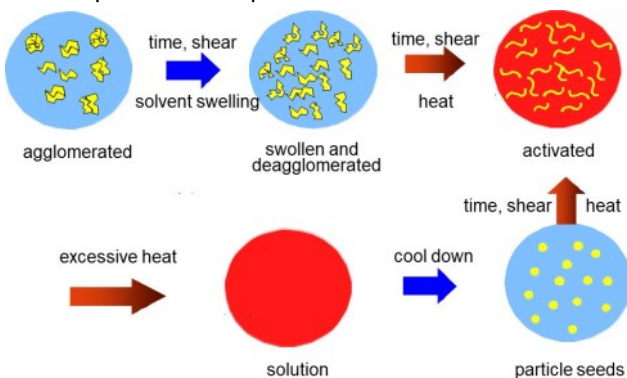


Figure 8: Mechanism seeding

During the cool down process, the solubilized wax is immediately coming out of the solution and is recrystallizing visible as large, weak particles, so called “seeds” and guides to a loss of fineness of grind (Hegman). The seeds, visualized in a grindometer based draw down test in *figure 10*, are typically distributed throughout the sample.

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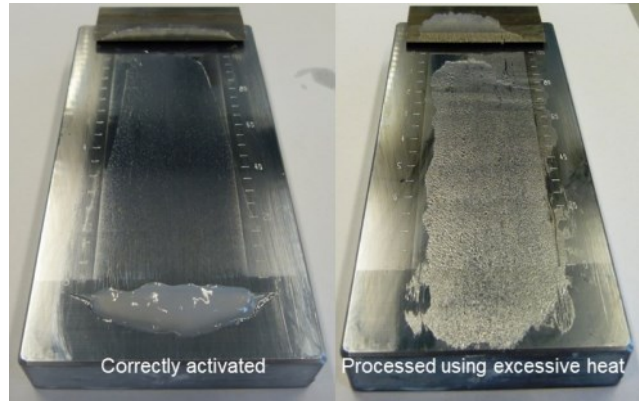


Figure 9: Visualizing seeding

To avoid classic seeding formation, a system individual temperature maximum should not be exceeded. However, in case seeding is appearing after the activation of organic thixotropes, the material is not necessarily lost. As this seeding is typically detected immediately after production, the material needs to be reprocessed at the relevant optimum activation temperature.

Another potential crystal forming phenomenon with organic thixotropes is the so called “latent seeding”. The mechanism is visualized in *figure 10*. This is typically the result of a too low temperature during processing. Consequently, due to too less solvency, proper softening and solvation of the wax particles is not guaranteed. The majority of the rheology modifier might be dispersed but a significant portion may not be converted into the required colloidal stage. Very little hard waxy particles, which are often containing totally undissolved and unsoften centers, are remaining.

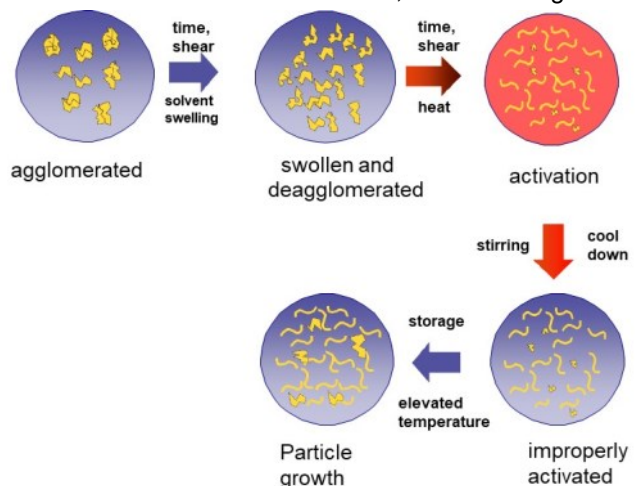


Figure 10: Mechanism latent seeding

The remaining particles are often small enough not to be detected using a grindometer initially after finishing production. However, as these type of seeds if growing with time, which will vary with the relevant storage temperature, it is often the case that the seeds are being detected after the material has already been refilled and shipped from the manufacturing plant.

Therefore, latent seeding is often much more problematic than classic seeding, in case the finished material needs to be recalled resulting in unnecessary added expenses. The effect of latent seeding can be observed with both classes of organic thixotropes, ricinus oil derivatives and diamide waxes.

Another side effect, which is mostly occurring when working with castor wax based rheology modifiers, is the so called false body. When activated correctly into the system, but cooled down without agitation excessively high viscosities will develop. This apparent viscosity rise can be avoided by cooling down under stirring after the activation process. This on the other hand means, that the possibility to fill and pack material equipped with castor waxes hot is quite limited.

As this effect might also occur on storage, in case readily produced material containing properly activated organic thixotrope is exposed to elevated temperature, e.g. by exposing to the sun. Under this conditions often an apparent rise of the in-can viscosity is observed. Such material can be easily re-processed by applying shear forces breaking down the viscosity to the normally adjusted level.

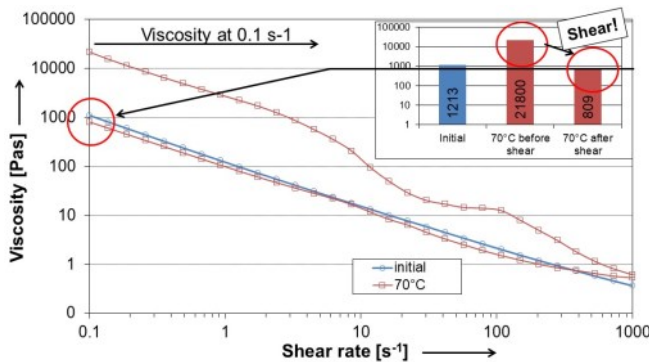
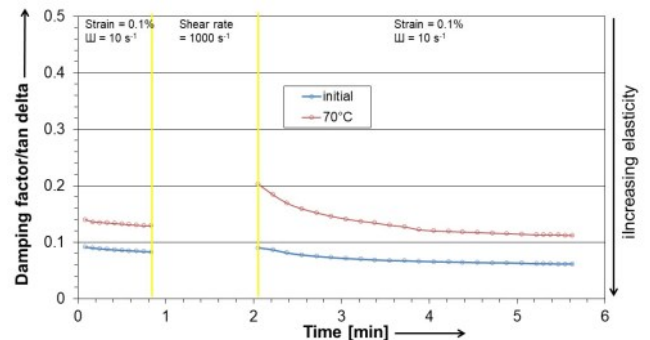


Figure 11: Rheology false body effect

In *figure 11*, the effect of false body up on the storage at elevated temperature of a system containing correctly activated castor wax is described. The material initially shows a low-shear viscosity, measured at a shear rate of 0.1 s^{-1} of approximately 1200 Pas. However, after storage at elevated temperature of 70°C , the viscosity has risen to about 22000 Pas. With shear the viscosity at low shear rates reduces to approximately the initial value.

Comparing the material without and present false body after storage at elevated temperature of 70°C in an oscillatory rheology test shows that the viscoelastic characteristics are only minorly affected. As visualized in *figure 12*, both samples, materials tested initially and after storage at elevated temperature of 70°C , are showing very similar damping factors. After breaking down all structure in step 2 by rotation, the tan delta values are immediately returning to the similar range within the strongly elastic dominated range. Therefore, as results of both graphs (*figure 11 and 12*), false bodies are only affecting the viscosity and do minorly change the viscoelasticity.



False body effects are not in all cases unwanted. It is also possible for certain systems to use false body effects in a positive way. This is for instance the case with automotive car body putties which are often being formulated with castor waxes, as false body effects are easily to adjust. The effect is used in this case to make material more „putty like“ appearing.

All described side effects such as false bodies and seeding, are caused by wrong use of the relevant organic thixotropes and do not describe a potential weakness of the product itself.

Formulating with organic thixotropes

As previously described, working with organic thixotropes is a quite complex process. Castor wax based additives, such as our THIXCIN[®] R or THIXATROL[®] ST, require very exact temperature control to provide strong thixotropy and high viscosities at low shear rates to solvent-free and solvent containing systems. With respect to solvent borne systems, the use of ricinus oil derivatives is limited to those systems of low to medium polarity. In case of improper processing, unwanted side effects such as seeding and false bodies are possibly occurring. Only false bodies are wanted in some specific systems, such as putties for automotive body repair.

Conventional diamide waxes such as THIXATROL[®] Max and THIXATROL[®] Plus are minimizing the risk of false bodies and classic seeding and can be applied in solvent borne systems of a wide polarity range including oxygenated media such as ketones and esters. However, for activation tendentially higher temperatures in comparison to castor waxes are required. These in certain cases quite high temperature requirements, are often the root cause for sometimes reported latent seeding issues which are caused by an under activation.

Consequently, the main reason for developing a new generation of organic thixotropes is related to the above described facts and should reduce the complexity in use. The latest products under the brand names THIXATROL[®] AS 8053, THIXATROL[®] PM 8054, THIXATROL[®] PM 8056 and THIXATROL[®] PM 8058 are offering the following listed benefits in comparison to commercially available grades:

- Tendentially lower activation temperature
- Stable viscosity build over a wide range of application temperatures
- Less temperature sensitivity
- Applicable for solvent based systems of low to high polarities
- Larger tolerance for process and raw material variations

This all guides to improved robustness under real life conditions in production of systems where a high viscosities at low shear rates and sag stability is needed. These can be typically adhesives and sealants as well as protective and marine coatings.

Appendix

Figure 1: Schematic representation of the flow characteristics provided by the various classes of rheology modifiers.

Figure 2: Chemical structure to display the hydrogenation of castor oil to create castor wax

Figure 3: Partial chemical formula of a diamide based wax

Figure 4: Schematic representation of the acting mechanism of a diamide based rheology modifier after correct activation.

Table 1: Overview of potentially recommended activation temperatures of different classes of organic thixotropes in various systems.

Figure 5: Schematic description of the activation mechanism of organic thixotropes

Figure 6: Result representation of a lab based ladder study to identify ideal activation temperature of castor wax based THIXCIN[®] R at a concentration of 1% in an aromatic free, alkyd based varnish.

Figure 7: Schematic visualization of the result of a lab based ladder study to identify the optimum activation time in relevance to the individually adjusted temperatures; tested in a solvent based alkyd system equipped with 1% castor wax based THIXATROL[®] ST.

Figure 8: Schematic description of the classic seeding mechanism during the activation of organic thixotropes.

Figure 9: Visualization of seeding as a grindometer draw-down. Tested in a paraffinic oil equipped with 1% of castor wax based THIXCIN[®] R.

Figure 10: Schematic description of the mechanism of latent seeding during and after the activation of organic thixotropes.

Figure 12: Rheology curve of a paraffinic oil equipped with 1% of THIXCIN[®] R before and after storage at elevated temperature of 70°C to visualize the occurring false body effect; determined using the Anton-Paar MCR 301 rheometer, equipped with PP 50 measuring geometry at a gap width of 1 mm, at a temperature of 23°C.

Figure 13: Viscoelastic data curve of a paraffinic oil equipped with 1% of THIXCIN[®] R before and after storage at elevated temperature of 70°C to visualize the occurring false body effect; determined using the Anton-Paar MCR 301 rheometer, equipped with PP 50 measuring geometry at a gap width of 1 mm, at a temperature of 23°C; tested as a 3 step test splitted in oscillation/rotation/oscillation.

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