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Organic Thickeners for Water-borne Paints

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Abstract: Thickeners are used in paint systems to achieve particular rheological properties such as shear-rate dependent behavior, to control the viscosity at low and high shear rates, sag resistance and application viscosity. This contribution addresses the use and application of thickeners in water-borne paints. Examples of successfully used types of thickeners are the cellulose and PUR-thickeners. Specific compositions, features and benefits of both types are explained in detail.

Keywords: Associative thickeners · Cellulose · Paint additives · Polyurethane · Thickeners

1. Introduction

Thickeners are used in paints and other coating materials to achieve particular rheological properties. The rheological properties relate to processing, storage and application conditions and are affected by all main components: binder, pigments, solvent, and additives.

Thickeners are added during the production process to obtain optimal flow behavior to the mill-base. If the pigments are dispersed in a medium which is too thin, a turbulent flow behavior occurs which leads to a great loss of the energy supplied, so it is not used in an optimal way for the dispersing process.

During storage, the paint should have a sufficiently high viscosity in order to prevent sedimentation of pigment particles.

In a similar way various application characteristic properties are determined by the viscosity adjustment, for example flow and leveling, sag resistance, brushability as well as film thickness and opacity [1].

Thickeners are used in both solvent-borne and water-borne paints. Various kinds of thickeners are in use:

- Organic thickeners
- Inorganic thickeners

Organic thickeners are used in both water-borne and solvent-borne coatings. Main representatives are cellulose derivatives and polyurethane thickeners; both are predominantly used in water-borne coatings. Main organic thickeners used in solvent-borne coatings are the polyamide-based and the hydrogenated castor oil-based thickeners. Organoclays are examples of widely accepted inorganic thickeners, mainly for solvent-borne paints. Organic thickeners differ from inorganic thickeners not only with regard to their composition but also in their specific properties and performance. Most organic thickeners are surface active; furthermore they may be part of the polymeric film matrix during film-formation. This explains, for instance, the excellent coating layer properties like, for example, improved appearance, gloss and flow. The variations regarding the chemical composition of these thickeners are extraordinary versatile.

For water-borne paints different types of organic thickeners are distinguished on the basis of thickening functionality: thickeners that just thicken the aqueous phase and products that thicken by interaction with other paint ingredients.

The following groups of products are products that only thicken the aqueous phase:

- Cellulose derivatives
- Starch derivatives
- Acrylic thickeners

Cellulose ethers are the most commonly used representatives of the aqueous phase thickeners and will be discussed more in detail in the next paragraph.

Starch-based thickeners are used in very high pigmented – pigment volume concentration (PVC) over 85% – low-cost paints and function as thickener as well as binder. The use of these paint systems has decreased significantly over the past few decades.

Acrylic thickeners are also used to a limited extent in wall paints, particularly for interior use. The advantage of these thickeners is that they are available in liquid form, as an emulsion or solution. The main drawback of acrylic thickeners is, however, that the thickening efficiency is strongly pH related. Furthermore, acrylic thickeners usually increase the water sensitivity of the paint layer.

In this presentation characteristic features of the two main groups of thickeners used for the formulation of water-borne paints will be highlighted: the classical cellulose-based thickeners and the more recently introduced PUR- or associative thickeners.

2. Characteristic Viscosity Profiles of Paints

The rheology behavior of a system under various conditions may be described by a viscosity profile, showing the viscosity as a function of the applied shear conditions [2].

Viscosity is a measure for the flow resistance with which a liquid resists its de-

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formation and is the quotient of the shear stress τ and shear rate D:

$$\eta = \frac{\tau}{D} = \frac{\text{Newton.sec}}{\text{m}^2} \text{ or Pascal·sec (Pa.s)}$$

Newtonian flow defines a system where viscosity is constant at the indicated pressure and temperature regardless of applied shear rate and time (Fig. 1). Therefore a single viscosity measurement will give a true value for the viscosity; the rate of shear is directly proportional to the shearing force. Examples for Newtonian liquids are water and pure solvents.

In the case of pseudoplastic flow viscosity decreases as shear rate increases. Various viscosity measurements are necessary across the shear rate range in order to establish a correct rheology profile. Almost all paints and varnishes show more or less pseudoplastic (shear thinning) flow behavior! The flow behavior of a substance is called thixotropic if its viscosity is reduced at a constant shear rate (or constant shear stress) with ongoing time; after ending the stress the viscosity increases again. Therefore thixotropy is time-dependent.

Various paint properties are related to typical shear conditions, as can be deduced from Table 1. Properties like sedimentation and flow and leveling are related to low shear forces. The lower the viscosity is at low shear range, the better the leveling; however, stability is favored by high viscosity at low shear, indicating that compromises have to be made by the paint formulator. The slope of the viscosity is largely related to the characteristics of the thickener used and therefore properties like flow and leveling, stability as well as properties during the application process.

3. Cellulose-based Thickeners

3.1. *Chemistry and Specific Properties*

Cellulose ethers have been used as thickeners for latex paints for many decades. Worldwide some 35000 tons of cellulose ethers are used annually as thickeners in emulsion paints [1].

The basic material from which these thickeners are made is cellulose. Cellulose is a polysaccharide and is made up of so-called anhydroglucose units that are linked by β-1,4-glycosidic linkages [3]

Each anhydroglycose unit contains three functional hydroxyl groups suitable

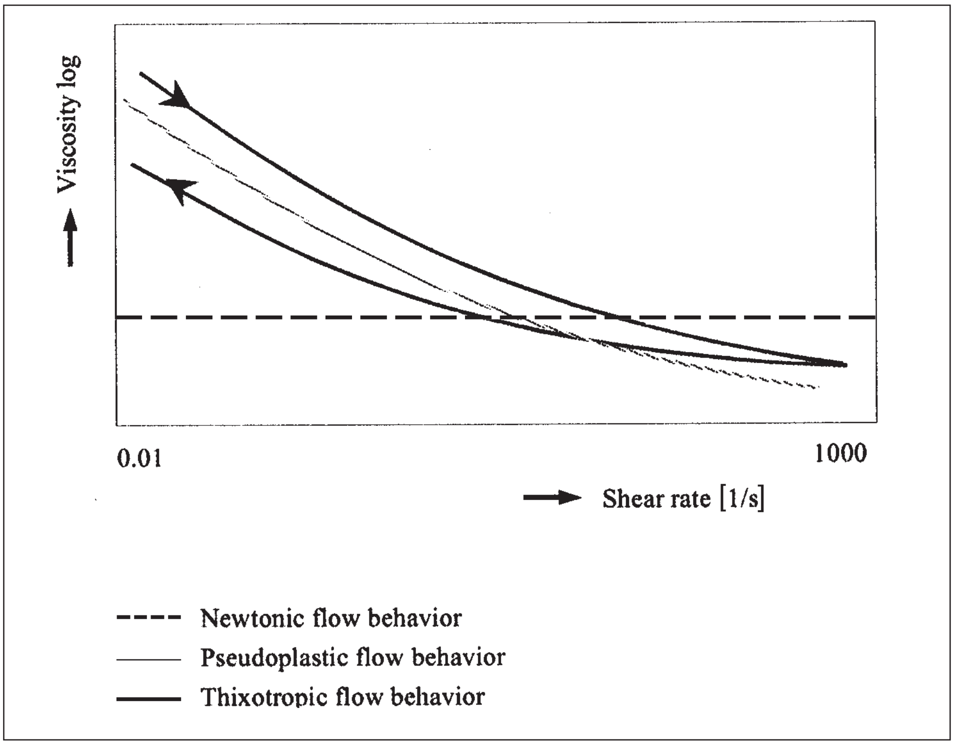


Fig. 1. Various viscosity profiles

Table 1. Typical shear rates for different processes in relation to paints

Process	Typical shear rate range D [s^{-1}]
Sedimentation of particles	10^{-6} ... 10^{-4}
Leveling	10^{-2} ... 10^{-1}
Sagging	10^{-2} ... 10
Dipping bath	10 ... 10^{2}
Brushing	10^{2} ... 10^{4}
Spraying	10^{3} ... 10^{6}
Pigment dispersing	10^{3} ... 10^{5}
Transfer of printing inks by roller	10^{4} ... 10^{6}

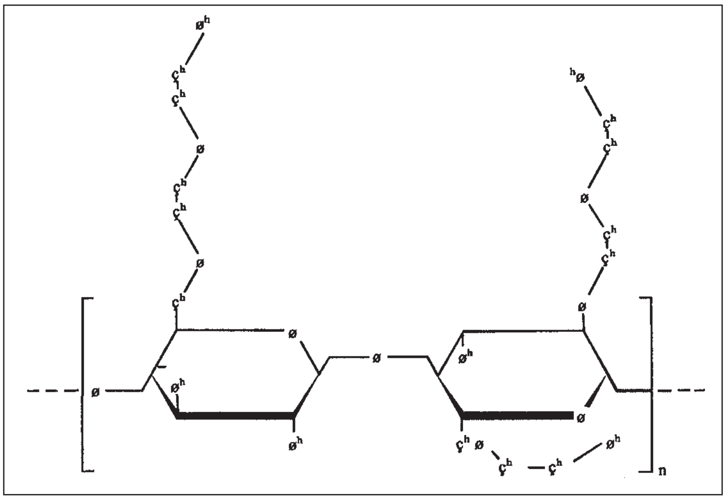


Fig. 2. Structure of hydroxy ethyl cellulose

for chemical modification. Modification is usually achieved through esterification. The method of modification largely effects the relative thickening properties and product features (Table 2).

Table 2. Influence of the various cellulose ether substituents on paint properties.

	Best result						**Worst result**
Pigment dispersion	HEC	>	CMC	>	EHEC	>	MHEC
Foam formation	HEC	=	CMC	<	EHEC	<	MHEC
Thickening properties	MHEC	>	HEC	>	EHEC	>	CMC
Storage stability	HEC	>	EHEC	=	MHEC	>	CMC
Bio stability	HEC	>	EHEC	>	MHEC	>	CMC
Brushability	HEC	>	EHEC	>	CMC	>	MHEC
Brush viscosity	MHEC	>	CMC	>	HEC	=	EHEC
Spatter resistance	MHEC	>	HEC	=	CMC	=	EHEC
Leveling	MHEC	=	CMC	>	HEC	=	EHEC
Sagging resistance	HEC	=	EHEC	>	CMC	=	MHEC
Water resistance	HEC	>	CMC	>	EHEC	>	MHEC
Color development	HEC	>	CMC	>	EHEC	>	MHEC
Scrub resistance	HEC	=	MHEC	=	EHEC	>	CMC

The most widely used cellulosic thickeners are:

Hydroxy ethyl cellulose (Fig. 2): HEC
Hydroxy propylmethyl cellulose: HPMC
Carboxy methyl cellulose: CMC
Ethyl hydroxy ethyl cellulose: EHEC

Obviously there is no 'ideal' cellulose ether in terms of paint properties, however, the influence of the substituent on the paint properties is quite significant. Best storage stability of the paint is achieved with HEC because of its very slight interaction with the pigment, extender, and binder of the paint. The storage stability is also improved by the fact that water is a very good solvent for HEC despite the presence of electrolytes and glycols. Cellulose thickeners are supplied as free-flowing powder and are typically used as a 2 or 3% aqueous gel.

3.2. *Thickening Mechanism of Cellulose-based Thickeners*

The thickening action of the cellulosic ether is more a function of its molecular weight than the choice of substituent. The influence of the molecular weight of the cellulose ether is summarized in Table 3. To keep it simple, paints with two different viscosities have been compared: a cellulose product with a 2% Brookfield viscosity of 6000 mPa.s and a product with a viscosity of 100 000 mPa.s. The higher the molecular weight of the cellulose product, the higher the thickening efficiency. A higher molecular weight does, however, produce an increased tendency to spatter, when the paint is applied by roller. The sensitivity to water is increased if a lower molecular weight is chosen

Table 3. Influence of the molecular weight of the cellulose ether on paint properties

	Best viscosity type
Thickening efficiency	100,000
Spatter resistance	6,000
Leveling	100,000
Sagging resistance	6,000 and 100,000
Hiding power	6,000
Application time	6,000
Brushability	100,000
Scrub resistance	100,000
Avoiding pigment flocculation	6,000

Cellulose thickeners thicken the water phase. The main contribution to the thickening is explained by the formation of chain entanglements between the dissolved cellulose molecules (Fig. 3) *via* intra- and intermolecular hydrogen bonding. Furthermore, the cellulose molecule is largely hydrated, which contributes to a reduction of the mobility of the water molecules, resulting in a higher viscosity.

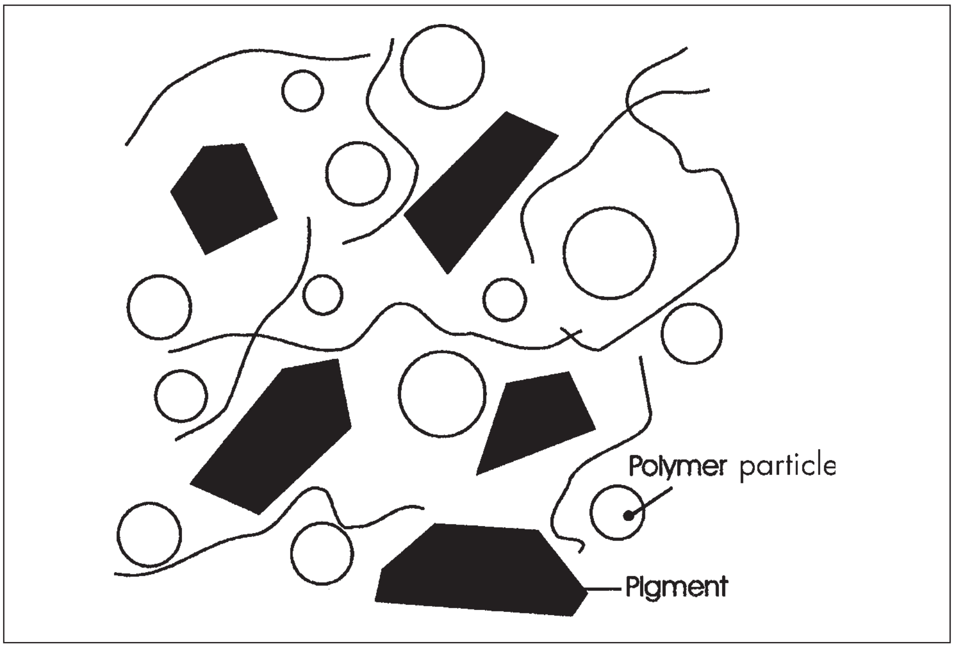


Fig. 3. Thickening mechanism: cellulose thickener, pigment and binder

Obviously the thickening effect is largely independent on interactions with other paints ingredients like the binder, pigment or extender.

This is a major difference in the mechanism of action between cellulose-based thickeners and the other most popular class of thickeners for water-borne paints, the associative thickeners.

The chain entanglements are relatively weak interactions and are deformed under shear conditions. The cellulose thickener molecules are re-orientated under shear conditions (including paint application conditions: brushing, rolling, spraying) forming parallel layers, which result in a lower viscosity of the paint ('shear-thinning'). The viscosity of associative thickened systems is less affected by shear (Fig. 4)

3.3. *Trade Products*

Natrosol: Aqualon
Methocel: DOW
Bermocoll: AKZO Nobel

4. PUR-thickeners

4.1. *Reasons for Development and Successful Acceptance*

The development of polyurethane- or PUR-thickeners is one of the most important advances in the area of rheological additives during last few decades. These thickeners, because of their thickening mechanism also known as 'associative thickeners', have become one of the most important types of thickeners for aqueous paints and coatings.

Compared to the traditionally used cellulose thickeners the application of these thickeners results in the best flow and leveling properties of the system.

Originally PUR-thickeners were recommended especially for low-PVC gloss emulsion paints because of the better leveling and appearance properties.

However, PUR-thickeners are also the preferred type of thickeners in other water-borne paints. They are, for example, of advantage in industrial coating systems because of their relative hydrophobic nature or in high-PVC emulsion paints, enabling the reduction of roller spattering during application.

The typical properties of water-borne paints, formulated with a PUR- thickener *versus* a similar paint but formulated with a cellulose resp. an inorganic thickener are presented in Table 4.

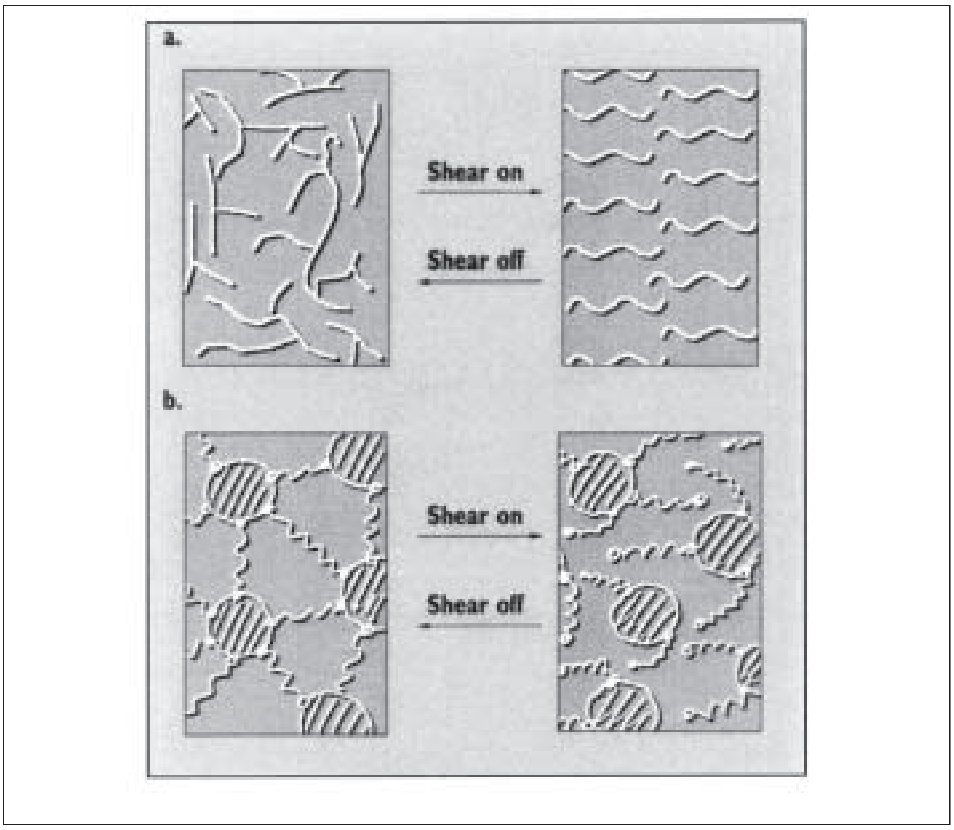


Fig. 4. The effect of shear on the structure of cellulose thickeners in comparison to an associative thickened system.

Table 4. Characteristic paint properties in relation to various types of thickener

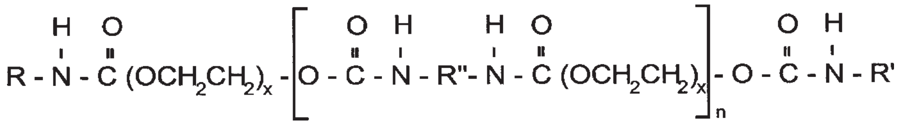
Property	PUR	Cellulose	Inorganic
Addition	++	+	--
Thickening efficiency	++	+++	+
Pigment stabilization	++	+	-
Bio stability	++	--	+++
Compatible with colorants	-	++	+
Application	+++	-	+
Alkydlike rheology	+++	-	--
Leveling	+++	-	--
Spatter resistance	+++	--	+
Sagging, settling	+	+++	+
Hiding power	+++	+	+
Water resistance	+++	-	+
Scrub resistance	+++	-	+
Gloss	+++	+	-

+++: very good
---- : very bad

4.2. *Chemistry of PUR-thickeners*

PUR-thickeners typically consist of nonionic low molecular weight polymers, typically between 10000 up to 50000. These thickeners are available either in liquid form, for example as a 50% solution in water or organic solvents, or in powder form.

The PUR-polymers are formed by reaction of di-isocyanates with diols and hydrophobically end-capped. The following chemical structure is a typical example in which R and R' represent hydrophobic, aliphatic or aromatic groups:



$$R-\overset{H}{N}-\overset{O}{C}(OCH_2CH_2)_x-\left[O-\overset{O}{C}-\overset{H}{N}-R''-\overset{H}{N}-\overset{O}{C}(OCH_2CH_2)_x\right]_n-O-\overset{O}{C}-\overset{H}{N}-R'$$

The following three segments can be distinguished in the molecule:

- hydrophobic terminal segments
- several hydrophilic segments
- urethane groups

Possible hydrophobic segments are, for example, oleyl, stearyl, dodecylphenyl and nonylphenyl. The composition of the hydrophobic segment is of great importance for the viscosity-increasing characteristics, especially the adsorption behavior.

Several molecule structures are possible; in practice especially PUR-thickeners with linear and comb-formed polymer structures have been accepted. The decisive factor for the viscosity increasing effect is that every molecule has at least two hydrophobic terminally captured segments. The hydrophilic segments R'' are polyethers or polyester. Examples are polyesters of maleic acid and ethylene glycol polyethers. Possible di-isocyanates are, for example, IPDI, TDI and HMDI.

The product properties of these PUR-thickeners are not only determined by these base components but also by the ratio of the hydrophobic and hydrophilic segments. Newest developments refer to 'high-shear PUR-thickeners'. These products affect mainly the high-shear viscosity and are characterized by low molecular weight and the presence of polyfunctional hydrophobic end-capped groups.

4.3. *Thickening Mechanism of PUR-thickeners*

The presence of hydrophobic and hydrophilic groups within the same molecule indicates a certain surface activity. Upon dissolution in water, formation of micelles does in fact occur above a characteristic concentration. In contrast to monomeric surfactants the same PUR-molecule may be present in more than one micelle.

In this way structures are formed which reduce the mobility of water molecules and increase the viscosity (Fig. 5). The hydrophobic segments within the molecule can adsorb onto the surface of the binder particles (the emulsion polymer) and eventually – depending on the characteristics of the surface – on the surface of solid particles like pigments and paint extenders, too.

The adsorption respectively association of the hydrophobic groups on the emulsion particles is of great importance to the thickening effect of PUR-thickeners. Owing to the formation of associations with emulsion particles, PUR-thickeners are also referred to as associative thickeners.

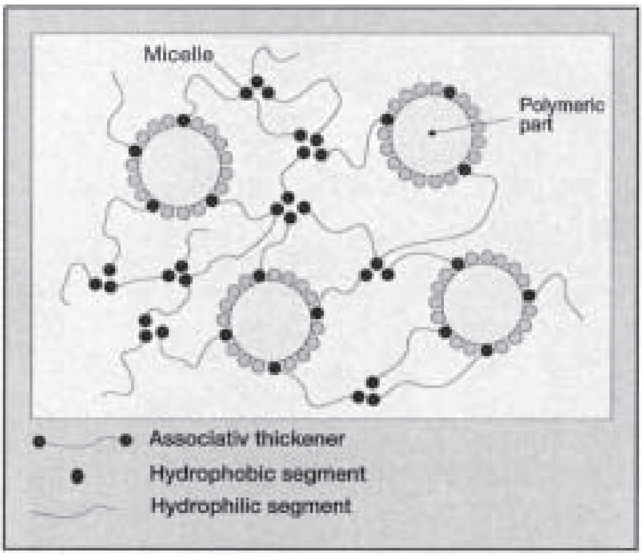


Fig. 5. Thickening model for associative thickeners

As each PUR-molecule has at least two hydrophobic segments it is possible for two emulsion polymer particles to be connected to one another through the PUR-molecule and therefore form a three-dimensional structure or network. In the same way the polymeric emulsion particle will be connected to the micelles formed by the PUR-thickener, which makes the structure denser.

The network results in immobilization of the liquid phase of the coating system and therefore leads to a viscosity increase. The extent of the association with the polymer particle depends on the characteristic properties of the hydrophobic group as well as on the surface properties of the polymer emulsion particles, the binder.

Consequently, systems with finer emulsions (larger total surface area) with PUR-thickener will be thickened more with PUR-thickeners than coarse emulsions. It has been proven that the number of bonds per molecule is proportional to the thickening effect under shear conditions.

The structure built up between the PUR-thickener and the emulsion particles is essentially resistant to mechanical influences, leading to virtually Newtonian flow behavior. The viscosity increase achieved with a PUR-thickener is the sum of the thickening effects, reached by following effects:

a) Increase in the viscosity of the water by dissolution of the PUR-polymer,
b) Micelle-formation and/or formation of connections between PUR-micelles,
c) Associations with emulsion polymer particles.

The relative contribution of the thickening effects to the thickening is expressed as follows:

$$\eta_t = \eta_o + \eta_a + \eta_m + \eta_p$$

in which:

η_t = final viscosity, mPA.s
η_o = initial viscosity
η_a = viscosity increase by interactions between polymer particles
η_m = viscosity increase by interactions between micelles
η_p = viscosity increase, dissolving PUR thickener in the aqueous phase

The contribution of η_p is negligible.

4.4. *Application Properties of PUR-thickeners*

A further classification for PUR associative thickeners may be made depending on the thickening effect in the mid-shear and high-shear range, in relation to the application in paints and coating materials:

'Mid-shear' PUR-thickener

These associative thickeners show a high viscosity increase within the medium shear section (10 up to 1000 s^{-1}) and the thickened systems show a nearly

Newtonian flow behavior and a great shear stability. Under higher shear conditions the network structure is only deformed slowly and the flow behavior is pseudo-plastic.

This effect is explained by desorption of PUR-thickener from the polymer particle surface. The extent to which these deformation processes result in a lower viscosity under shear conditions depends on the strength of association of the PUR-thickener molecules onto the polymer particle.

'High-shear' PUR-thickener

These thickeners show better shear resistance than the mid-shear PUR-thickeners and more shear stable emulsion paints can be formulated.

High-shear PUR-thickeners show best performances in the shear range from about 1000 s^{-1} onwards. These thickeners contain end-capped multifunctional hydrophobic segments that are strongly adsorbed onto emulsion polymer particles (Fig. 6).

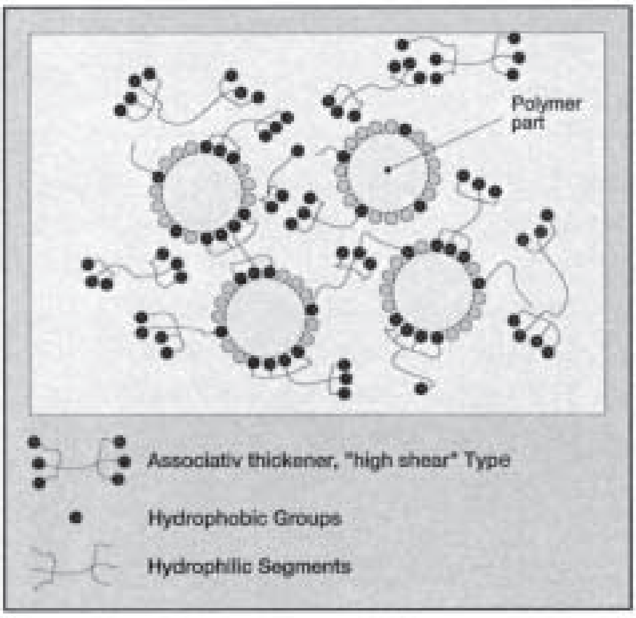


Fig. 6. Thickening model for high-shear PUR-thickeners

The thickening effect in the mid- and low-shear ranges quite is low, compared to for instance the above-mentioned mid-shear thickeners; high-shear thickeners can be used in conjunction with mid-shear or low-shear thickeners.

Polyurethane thickeners enable the formulation of water-borne paints and coatings with rheological properties that are virtually identical to those of solvent-borne alkyd paints. As described in the previous paragraphs, the structure formed between the PUR-thickener and the emulsion particle is to a large extent stable against mechanical influences resulting in almost Newtonian flow behavior (Fig. 7). Properties such as brush-drag during application, flow and leveling as well as film properties like film thickness will be optimized using PUR-thickeners instead of more classical thickeners like conventional cellulose thickeners.

PUR-thickeners prevent spattering during roller application. This is due to the relatively low molecular mass of the PUR-thickener molecule and consequently the low degree of elastic flow behavior. Precisely because of the low tendency to spatter, PUR-thickeners are being used in mid and high pigmented emulsion paints; in order to optimize the sag resistance of these high loaded systems; often a combination with a low shear thickener such as cellulosic or acrylate thickeners is preferred. For these systems the better flow characteristics are less a factor using PUR-thickeners (Fig. 8).

The final viscosity is achieved only after the association interactions with the emulsion particles and micelles are in equilibrium. A certain maturation time is required, which may vary from 2 h up to 2 d, depending on the characteristics of the thickener and emulsion. In order to optimize the viscosity for a particular system first the high shear viscosity is adjusted; this viscosity is to some degree directly proportional to the thickener concentration, up to a maximum which is characteristic for the system. The mid and low shear viscosity are subsequently adjusted.

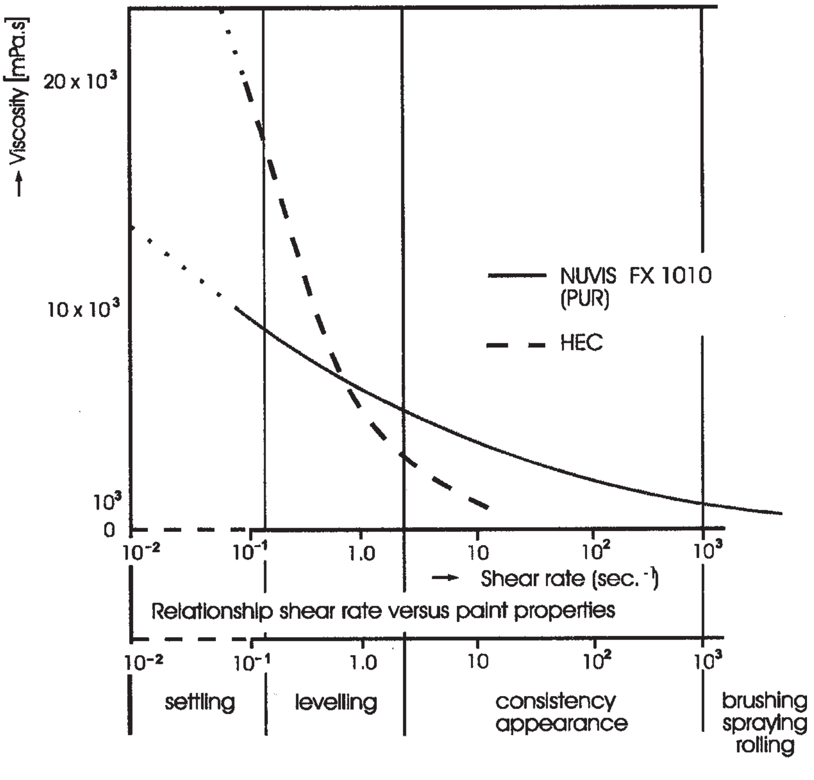


Fig. 7. Viscosity profile of an emulsion paint based on PUR-thickener *versus* HEC.

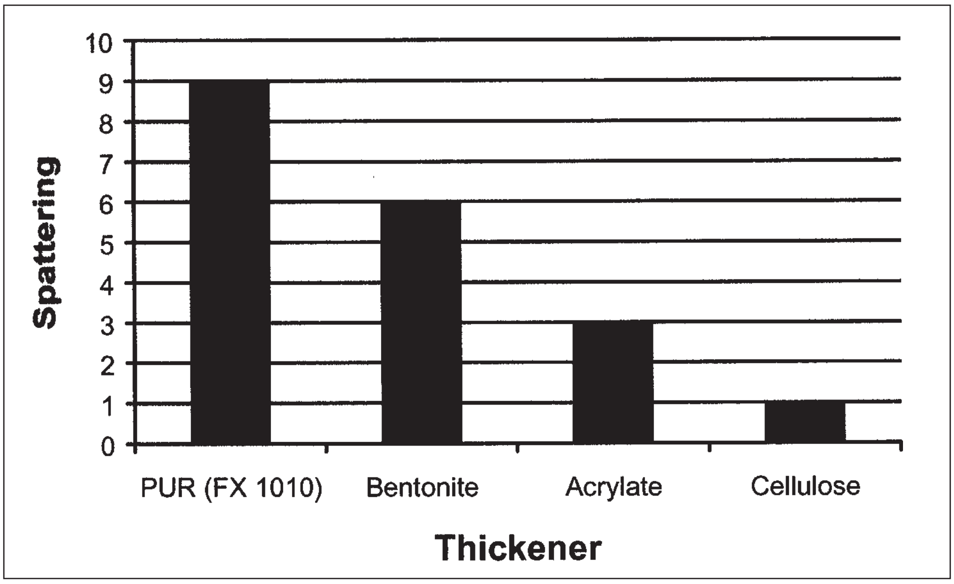


Fig. 8. Effect on roller spattering. Scale: 10= no spattering, 1= strong spattering.

4.5. *Interaction of Paint Ingredients and PUR-thickeners*

Many components that are normally used for the production of paints and coating materials influence the effect of PUR-thickeners. From the described thickening model it is clear that in particular the components that influence the association between the PUR-thickener and the emulsion particle as well as the micelle formation, will also influence the thickening achieved by the PUR-thickener.

Some common interactions are with following ingredients:

- Surface active agents, which are used to stabilize the emulsion polymer particles. These surfactants directly compete with the PUR-thickener regarding association processes. It is also possible that the PUR-thickeners are directly adsorbed onto the polymer particles *via* the surfactant molecules.
- Water-soluble, organic solvents like ethylene glycol, propylene glycol, glycol ether *etc.* impair micelle-formation because the differences in interfacial tension between micelle and continuous (water) phase are reduced, which means the number of micelles and hence their contribution to structure-formation decreases as well.
- Dispersing agents like low-molecular mass polyelectrolytes like polyacrylate salts are usually used in waterborne paints and coating materials for dispersing and stabilization of the pigments. According to the DLVO theory polyelectrolytes increase the number of molecules present in one micelle. That means that the number of micelles decreases as well as the number of bridges between micelles and micelle/emulsion particle. Consequently the density and strength of the structure is reduced.
- Water-insoluble coating additives, like coalescing agents or anti-foaming agents, in general have a viscosity-increasing effect. Since these products are dissolved in the micelles, the volume of each micelle increases; hence the distance between a micelle and a polymer particle decreases. Consequently also low-molecular mass fractions of the PUR-thickener can take part at the bridging and structure formation, leading to a strengthening of the structure and hence a viscosity increase. Next to this contribution, coalescing agents and co-solvents may soften the surface of the polymer particles and therefore increase the possibilities of an adhesion or adsorption of the hydrophobic groups of the PUR-molecule.

4.6. *Trade Products*

NUVIS FX 1010 (Sasol Servo BV)
NUVIS FX 1070 (Sasol Servo BV)
NUVIS FX 1025 (Sasol Servo BV)
Borchigel L 75N (Bayer AG)
Coatex BR 100 (Coatex SA)
Primal RM 825 (Rohm & Haas)

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