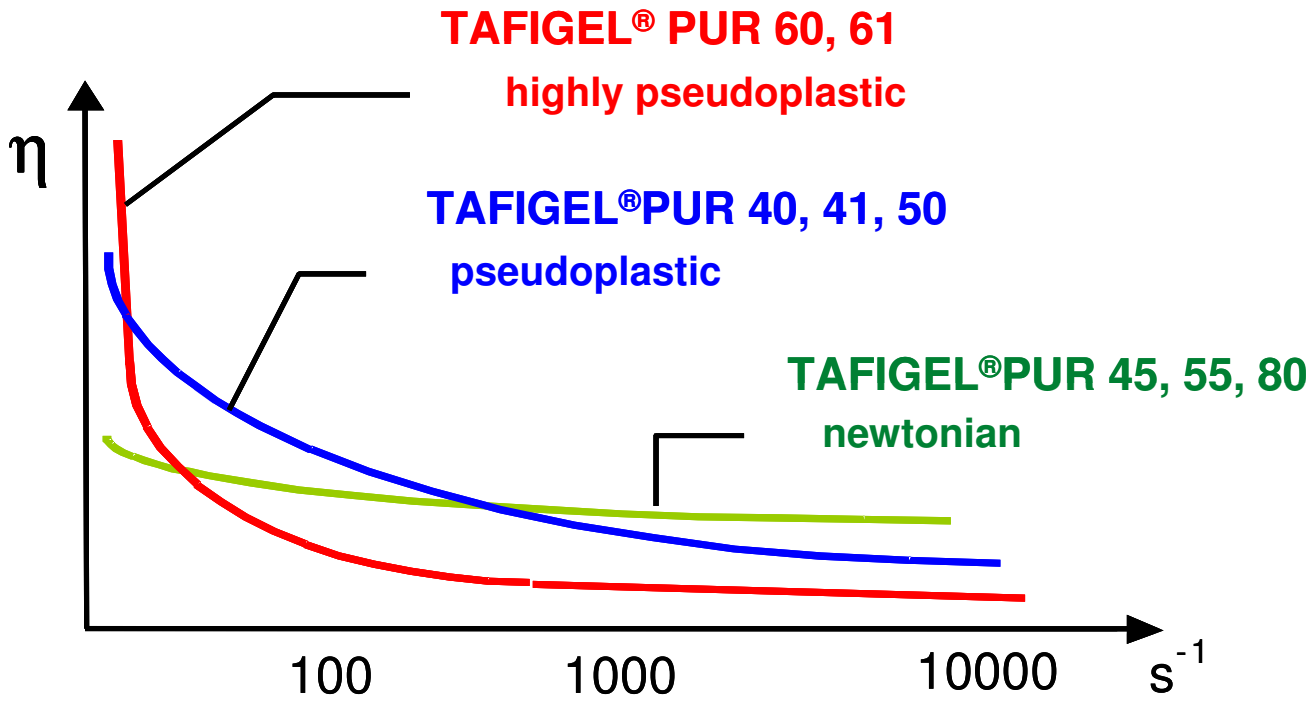
MÜNZING
CREATING ADDITIVE VALUE

Rheology Modifiers

TAFIGEL®

1	**Overview**	Page 3
2	**Typical rheology profiles**	Page 6
3	**Structures of associative thickeners**	Page 7
4	**Thickening mechanism**	Page 9
5	**Properties of polyurethane thickeners (HEUR)**	Page 10
5.1	Molecular weight	Page 10
5.2	Rheology profile	Page 10
5.3	Rheology control	Page 11
5.4	Influence of polymer emulsions	Page 12
5.5	Influence of pH	Page 13
5.6	Influence of solvents	Page 13
5.7	Influence of wetting agents	Page 17
5.8	Influence of solids	Page 19

TAFIGEL® PUR - Rheology Modifiers for waterborne paints, lacquers, adhesives and related systems



for improvement of:

- **Gloss**
- **Levelling**
- **Sag**
- **Edge hiding**
- **Spatter**
- **Brush drag**
- **Atomization**

TAFIGEL® PUR thickeners of MÜNZING CHEMIE GmbH are designed to cover a wide range of viscosity profiles. Focus is on good application properties, ease of incorporation and positive influence on properties of the formulation like gloss, water resistance etc.

1 Overview

1.1 Solvent free TAFIGEL® PUR thickeners

There exist three main groups of rheology modifiers: solvent free TAFIGEL thickeners, VOC free TAFIGEL thickeners and the classical TAFIGEL thickeners with high content of active substance. In every group thickeners with different rheological profiles exist.
TAFIGEL PUR 50 and TAFIGEL PUR 55 are solvent free thickeners.

	TAFIGEL® PUR 50	TAFIGEL® PUR 55
Rheology profile	pseudoplastic	newtonian
Active content	20%	20%
Emulsion	water	water
Application	• paints • lacquers • emulsion plasters • parquet lacquers • adhesives • printing inks • leather finish • alkyd emulsions	• parquet lacquers • gloss paints • printing inks • adhesives
Properties	**solvent free**	**solvent free** alone or in combination with other TAFIGEL PUR thickeners to increase high shear viscosity
Incorporation	can be added any time without predilution	can be added any time without predilution

Table 1: Range of solvent-free TAFIGEL® PUR thickeners

1.2 VOC free TAFIGEL® PUR thickeners

The second group are TAFIGEL thickeners which are free of volatile organic compounds. Additionally, they are also free of APEO compounds. The ease of incorporation was improved and even the TAFIGEL PUR 61 with a highly pseudoplastic rheology can be easily added without previous dilution.

	TAFIGEL® PUR 41	TAFIGEL® PUR 61
Rheology profile	pseudoplastic	strongly pseudoplastic
Active content	27%	25%
Application	• paints • lacquers • emulsion plasters • parquet lacquers • adhesives • printing inks • leather finish • alkyd emulsions	• thick film systems • airless application • emulsion plasters • paints based on Vinylacetate-Copolymers, PU-emulsions or alkyd emulsions
Properties	• **VOC free** • very easy incorporation	• **VOC free** • easy incorporation
Incorporation	can be added any time without predilution	can be added any time without predilution the preparation of a master batch can facilitate handling

Table 2: Range of VOC free TAFIGEL® PUR thickeners

1.3 TAFIGEL® PUR thickeners with high active content

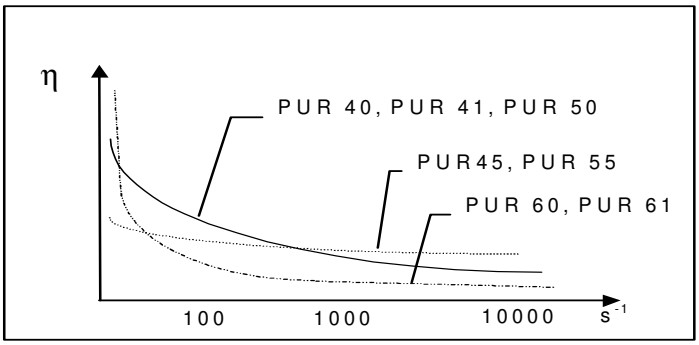
In the third group the thickeners with high content of active substance are included. These rheology modifiers cover the whole range of newtonian, pseudoplastic and highly pseudoplastic thickeners.

	TAFIGEL PUR 40	TAFIGEL PUR 45	TAFIGEL PUR 60
Rheology profile	pseudoplastic	newtonian	strongly pseudoplastic
Active content	40%	40%	40%
Emulsion	butyl triglycol/water	butyl triglycol/water	butyl triglycol/water
Application	• paints • lacquers • emulsion plasters • parquet lacquers • adhesives • printing inks • leather finish • alkyd emulsions	• parquet lacquers • gloss paints • printing inks • adhesives	• thick film systems • airless application • paints based on Vinylacetate-Copolymer • paints based on PU emulsions and alkyd emulsions • emulsion plasters
Properties	classical product of universal rheology and properties	alone or in combination with other TAFIGEL PUR thickeners to increase high shear viscosity	unique product for thick layers, spray applications and resins which are difficult to thicken
Incorporation	can be added any time without predilution	can be added any time without predilution	should be added to the grind or after pre-cutting with butyl-triglycol/water (25/75) or Dowanol DPM

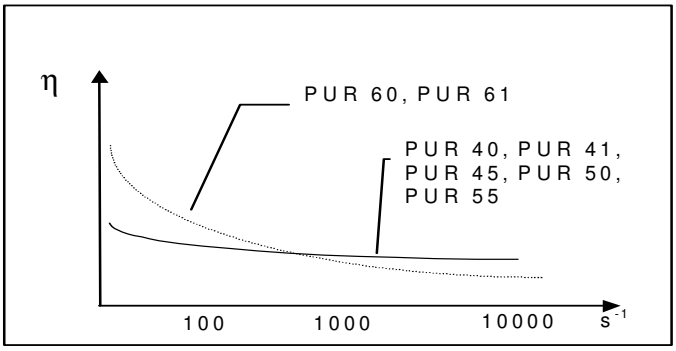
Table 3: Range of TAFIGEL® PUR thickeners with high content of active substance

2 Typical rheology profiles

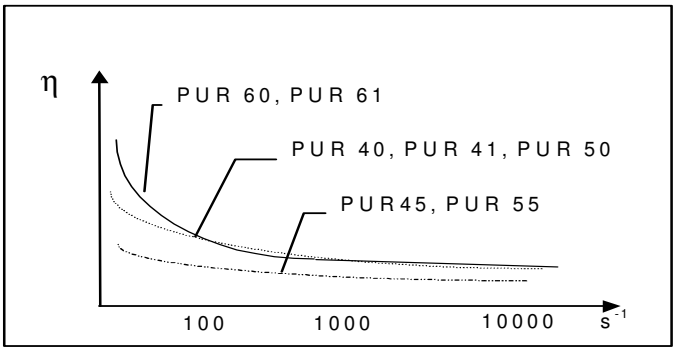
in acrylic-(copolymer) emulsion



in polyurethane emulsion



in VAc-(copolymer) emulsion



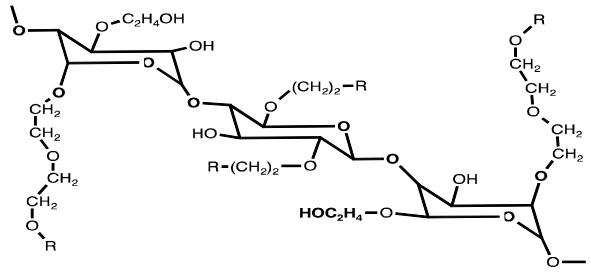
3 Structure of associative thickeners

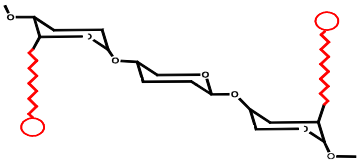
3.1. Different types of associative thickeners

TAFIGEL® - hydrophobically modified ethoxylated urethane copolymer (HEUR)

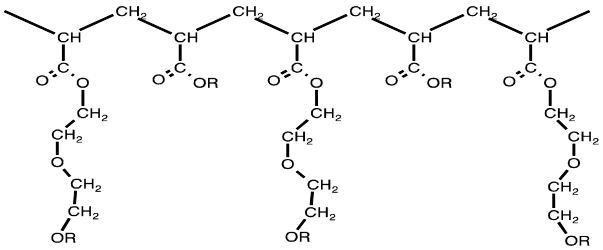
other types - hydrophobically modified alkali swellable emulsions (HASE)

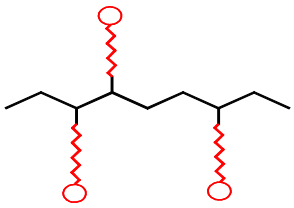
- hydrophobically modified cellulose ethers (HMHEC, HMC)
- combinations of HEUR and ASE



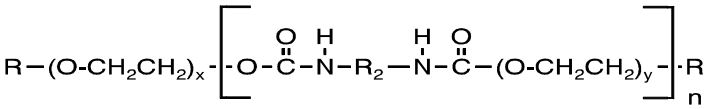


HMHEC





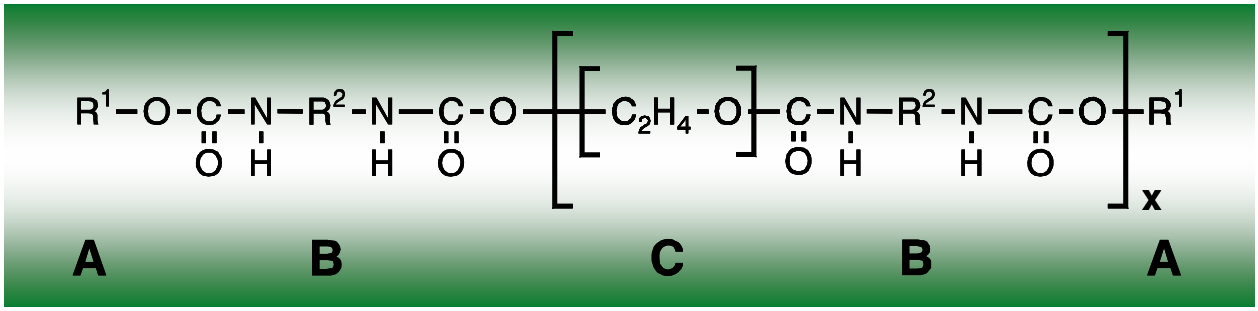
HASE



HEUR

Hydrophobic groups

3.2. Schematic structure of Polyurethane Thickeners (HEUR)



Type and function of the molecule parts A, B, C:

A: Hydrophobic end groups (= **R^1**)

e.g. long alkyl chain hydroxy or amine compounds. Hydrophobe-hydrophobe interactions between these groups and adsorption onto non-polar molecule surfaces (emulsion, pigments) result in formation of a three dimensional network

B: Urethane-Groups

Links in the thickener between molecule parts A and C. Can form hydrogen bonds (**R^2** e.g. C_6H_{12})

C: Polymer backbone

Provides water compatibility of the thickener and formation of hydrogen bonds

4 Thickening Mechanism

Polyurethane thickeners form aggregates (micelles) due to their hydrophobic-hydrophilic-hydrophobic structure. One thickener molecule can participate in two or more micelles. Micelles are linked together physically, i.e. individual thickener molecules form micelles with other thickener molecules and also interactions with hydrophobic emulsion particles or other hydrophobic formulation ingredients. The association immobilises these components and thus leads to the thickening effect. (Figure 1)

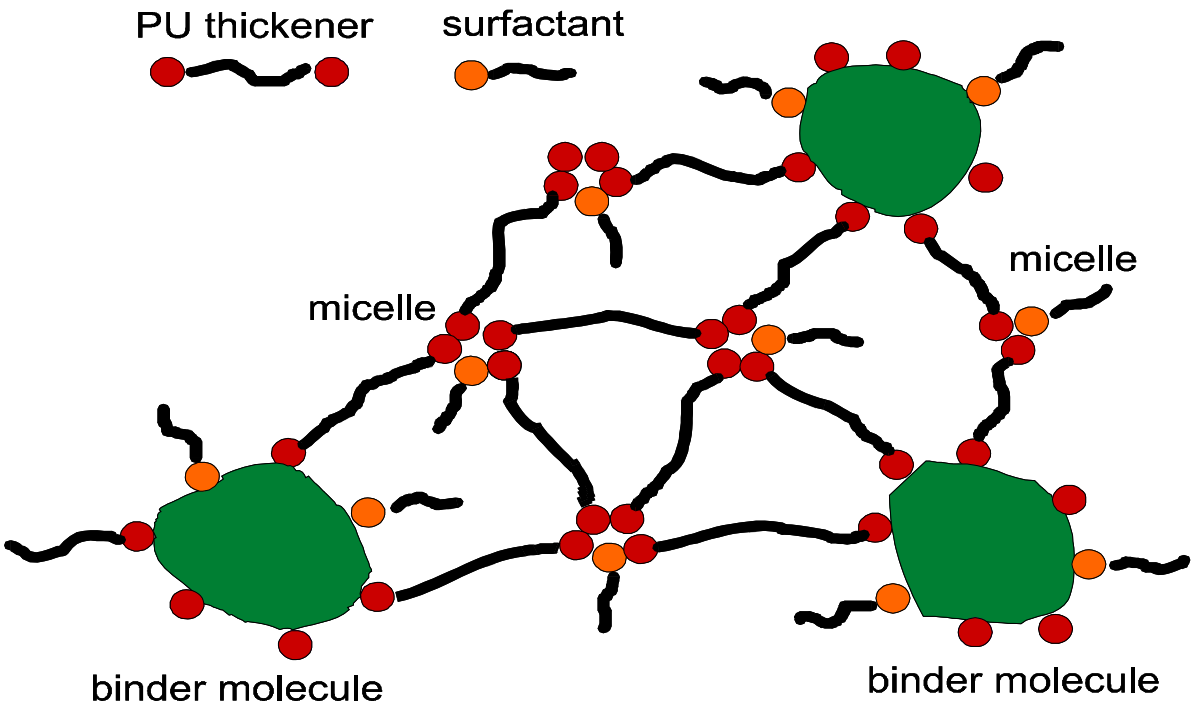


Figure 1: Formation of a three dimensional network

In some cases polyurethane thickeners act as dispersants or wetting agents. Depending on the kind of pigment hydrophilic and hydrophobic parts of the thickener molecule may interact.
The interaction of thickener molecules with pigments and extenders has a positive influence on settling and rub out.

5 Properties of Polyurethane Thickeners (HEUR)

5.1 Molecular weight

	Molecular weight (approx.) [g/mol]
Wetting agents/Surfactants	~ 10^2
Dispersing agents	~ 10^3 - 10^4
Polyurethane thickeners	**~ 10^4**
Acrylic thickeners	~ 10^5
Cellulose ethers	~ 10^6

Generally the molecular weight of polyurethane thickeners is significantly lower compared with other thickener types like acrylic thickeners or cellulose ethers. So are the elastic properties of polyurethane thickeners resulting in less spatter when used in emulsion paints.

5.2 Rheological profile

Rheological profiles of formulations can be adjusted by TAFIGEL® thickeners ranging from highly pseudoplastic to nearly newtonian. Thus the formulation properties can be influenced directly (Figure 2).

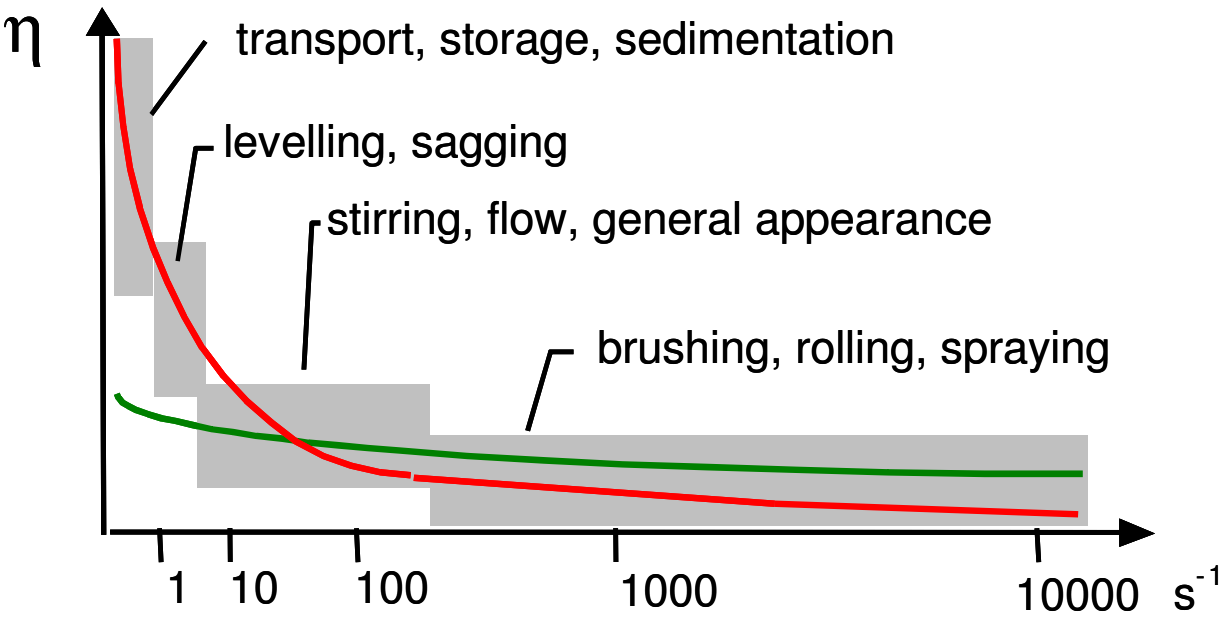


Figure 2: Relation between rheology and formulation properties

5.3 Rheology control

The associative properties of a polyurethane thickener is determined by the chemical nature and composition of the segments in the thickener molecule. E.g. shorter hydrophobic end groups may provide more newtonian flow behaviour.

The addition of newtonian thickeners TAFIGEL PUR 45 or PUR 55 to pseudoplastic types like TAFIGEL PUR 40, PUR 50 and PUR 60 can increase the viscosity in the high shear range (Fig. 3).

Combination of PUR thickeners

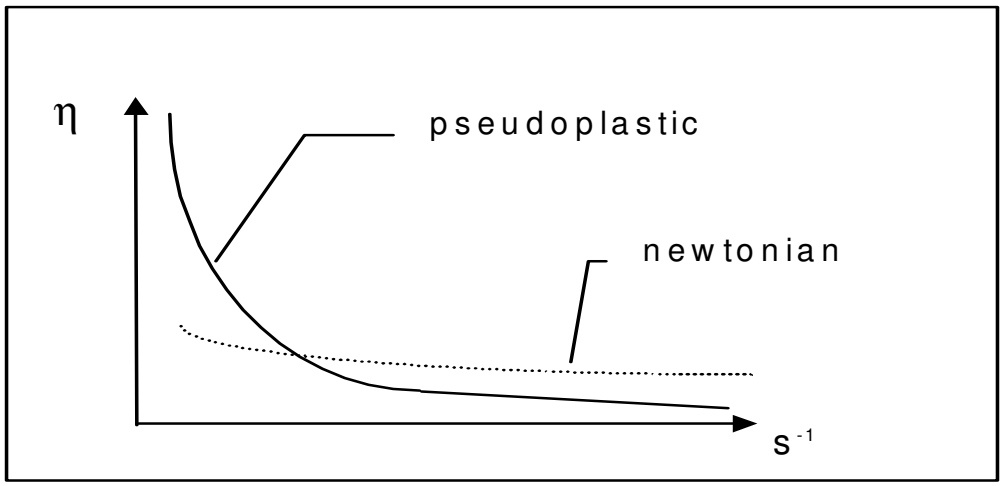


Figure 3: Combination of PUR thickeners with different rheologies

The advantages of these combinations are:

- less spatter on brush or roller applications
- increased brush drag, film build and edge hiding

The viscosity can be increased in the low shear range to provide:

- high anti-sag
- good atomisation for spray application

5.4 Influence of polymer emulsions

The obtainable rheology profile with polyurethane thickeners in emulsion systems depends on the kind of emulsion and other factors which will be discussed in this chapter. The figures 4 and 5 show the viscosity build with increasing dosage of TAFIGEL PUR 40 to acrylic emulsions (figure 4) and to styrene-acrylic and PU emulsions (figure 5).

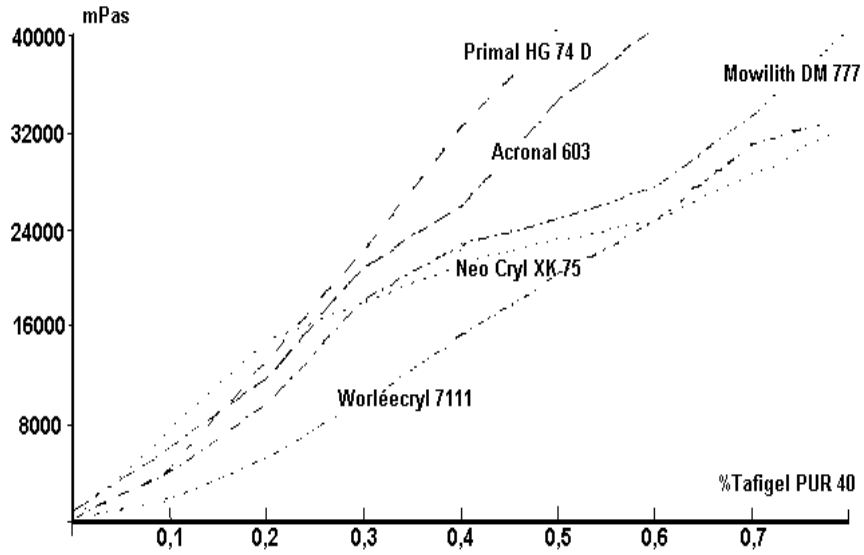


Figure 4: TAFIGEL PUR 40 in acrylic emulsions

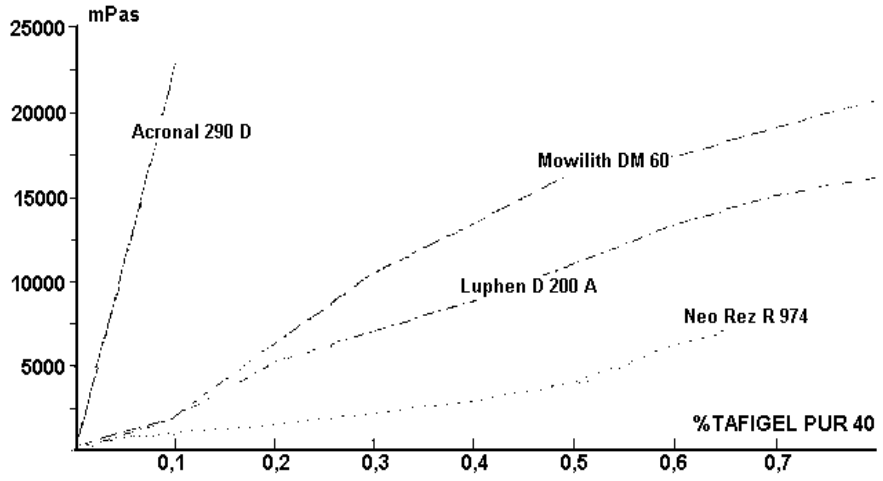


Figure 5: TAFIGEL PUR 40 in styrene-acrylic and PU emulsions

5.5 Influence of pH

Polyurethane thickeners can be used over a wide pH range (Figure 6).

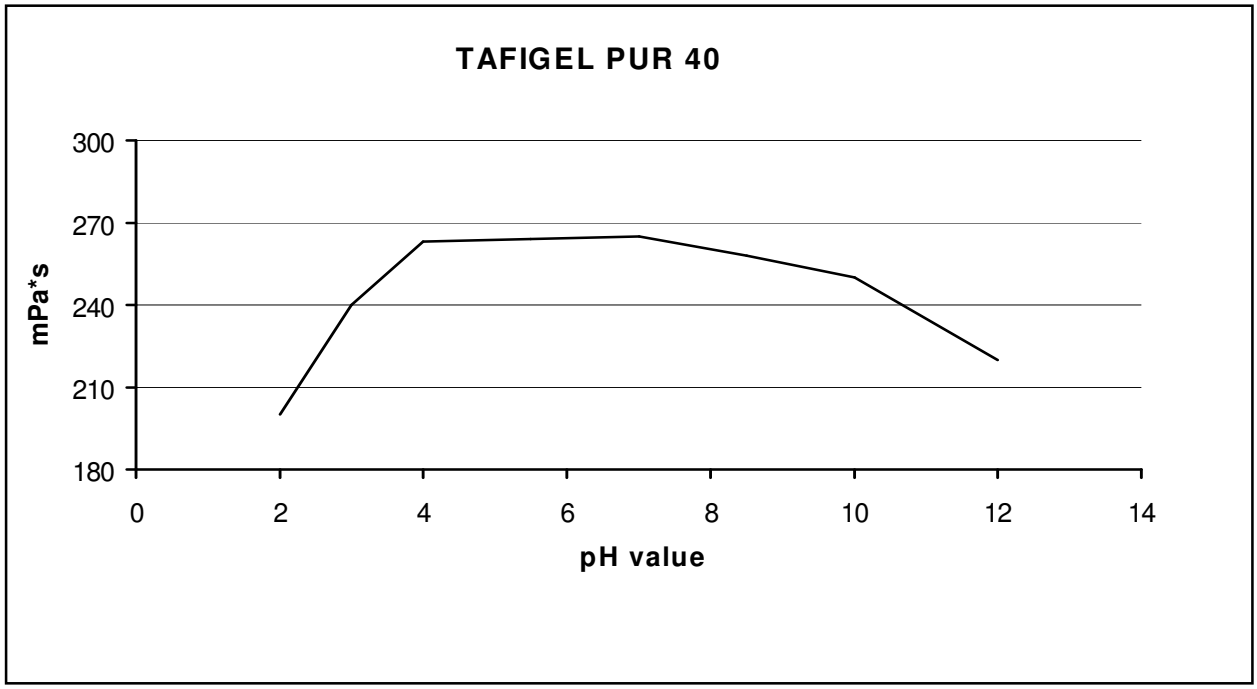


Figure 6: Influence of the pH value on the viscosity
(2% thickener solution in water)

Polyurethane thickeners show a very good resistance to hydrolysis. In acid emulsions it may be necessary to dilute the thickener before addition (i.e. 10% solution) to prevent coagulation of the emulsion.

5.6 Influence of solvents

The properties of polyurethane thickeners can be influenced by solvents, depending on type and quantity. Water soluble solvents generally decrease the viscosity, mainly in the low shear range. The continuous phase is changed, favouring the desorption of thickener molecules from emulsion particle surfaces and hindering thickener-thickener association. Water insoluble solvents increase the viscosity mainly in the low shear range. Water insoluble solvents participate in the hydrophobic-hydrophobic interactions and/or swell emulsion particles. (Figure 7).

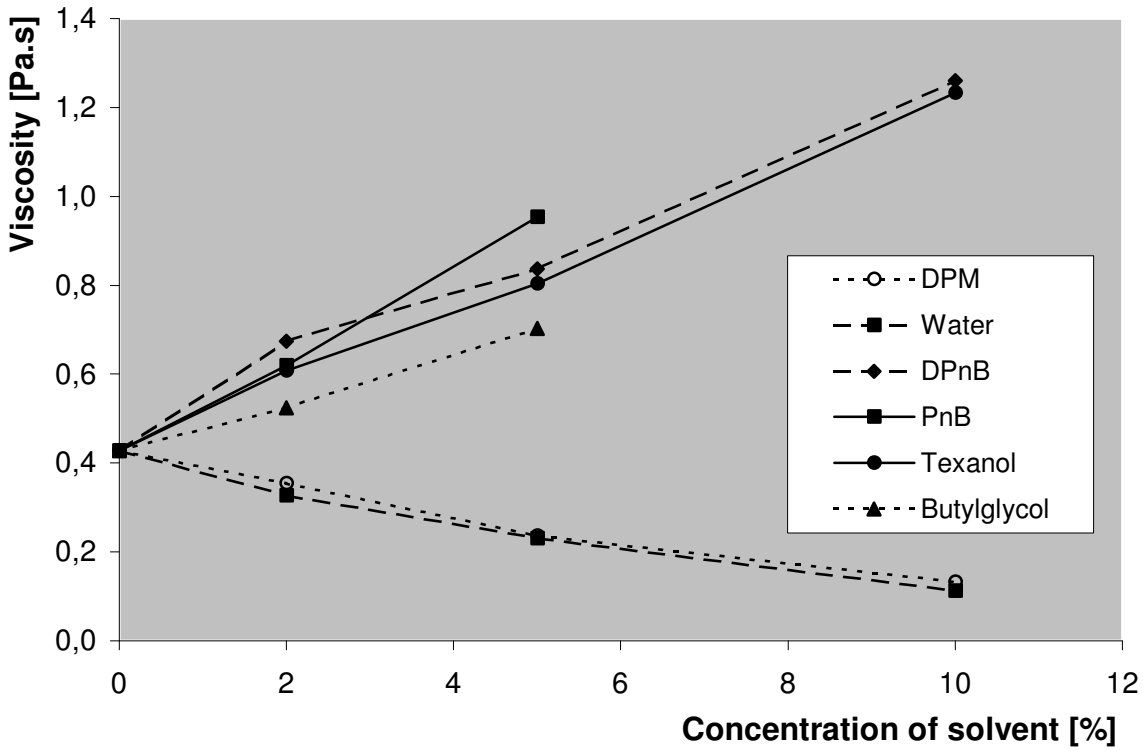


Figure 7: Influence of solvents on viscosity

These general statements, however, do not apply in all cases. Interactions of single components may be not predictable. Water soluble solvents as well may lead to an increase in viscosity. In Figures 8 and 9 the TAFIGEL PUR 45 with water and ethyl diglycol addition shows the expected newtonian rheology whereas with propylene glycol a pseudoplastic rheology is obtained. The pseudoplastic thickener TAFIGEL PUR 50 in presence of propylene glycol shows the opposite behaviour. The rheology with propylene glycol in those emulsions can be shifted towards newtonian behaviour (Figures 10 and 11).

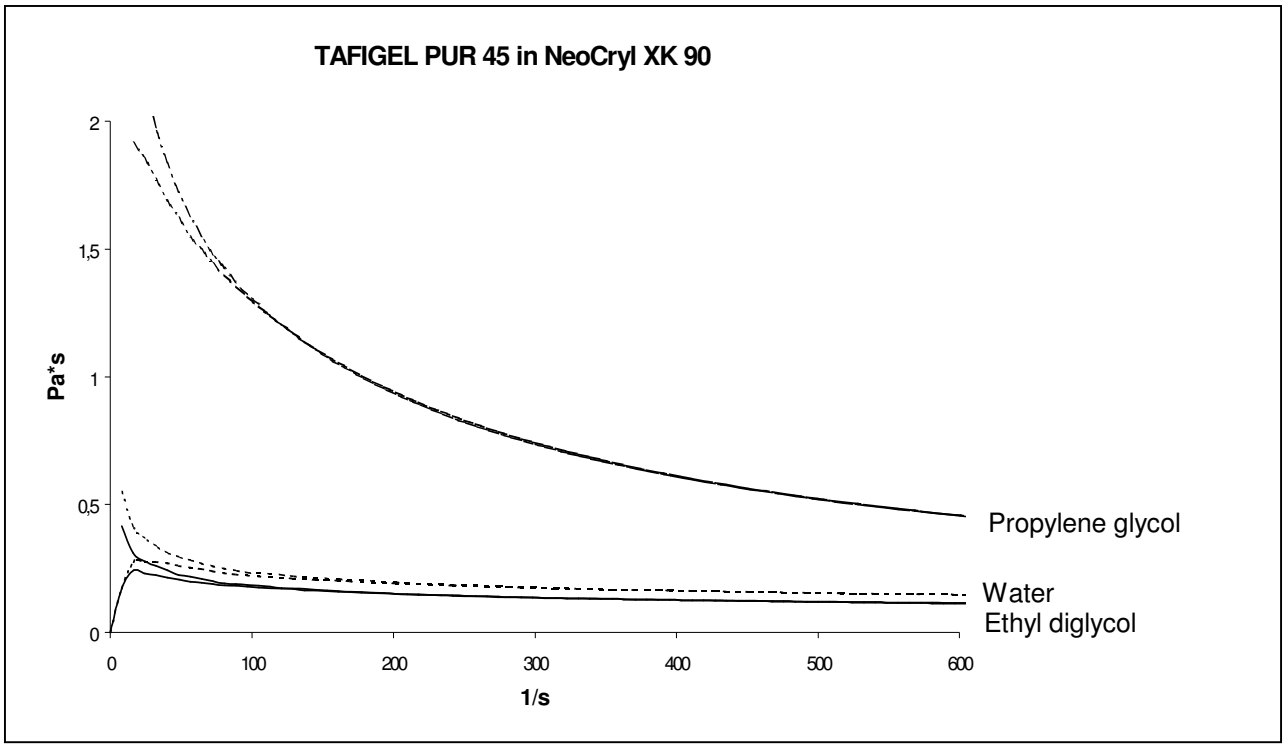


Figure 8: TAFIGEL PUR 45 in NeoCryl XK 90

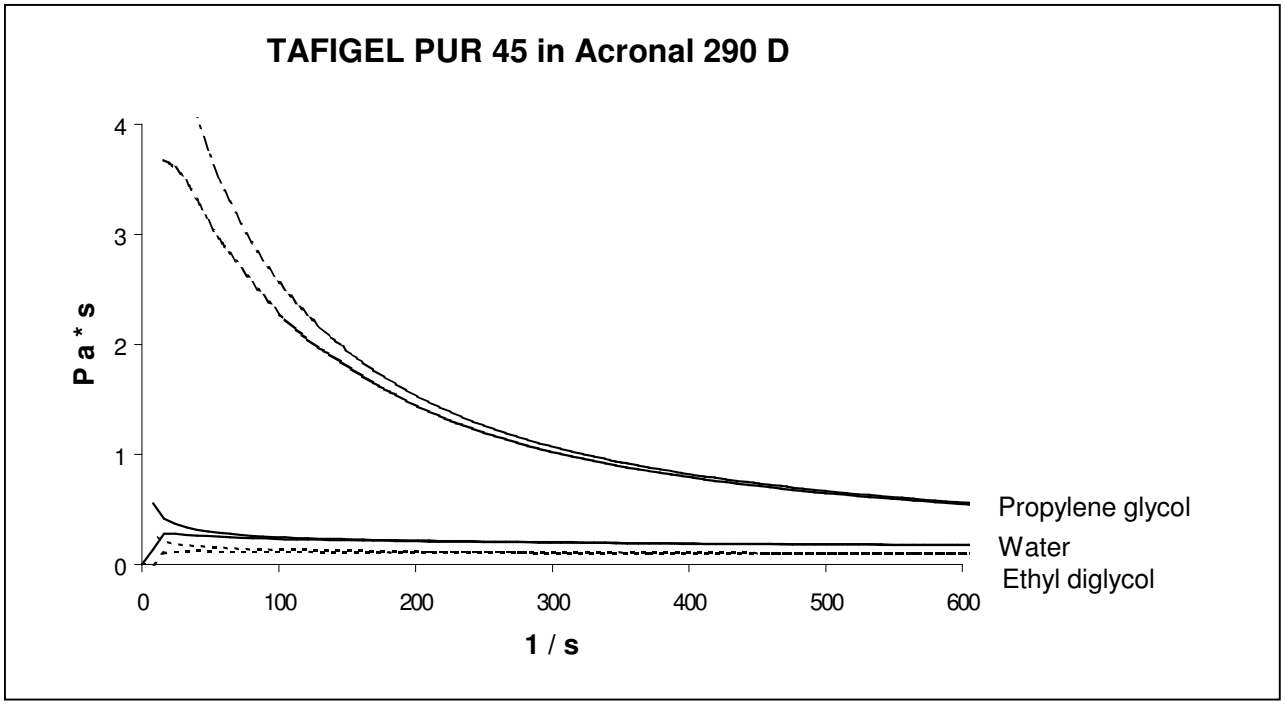


Figure 9: TAFIGEL PUR 45 in Acronal 290 D

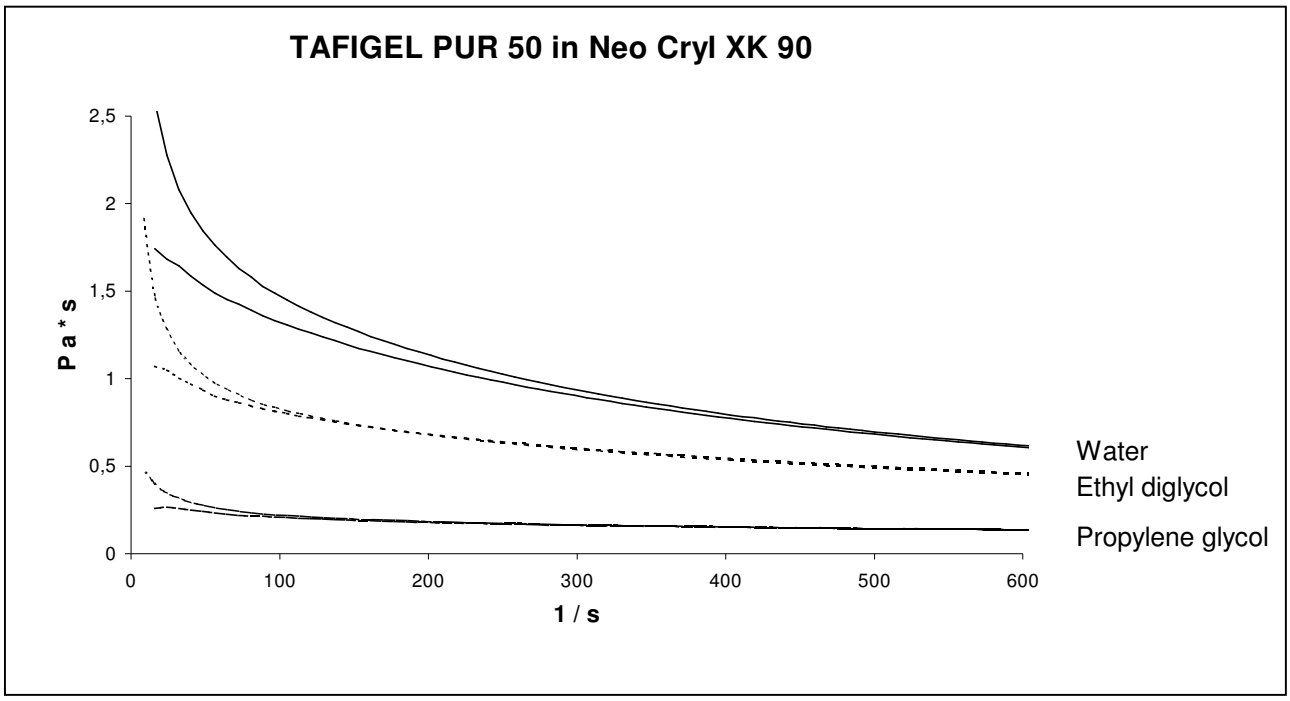


Figure 10: TAFIGEL PUR 50 in NeoCryl XK 90

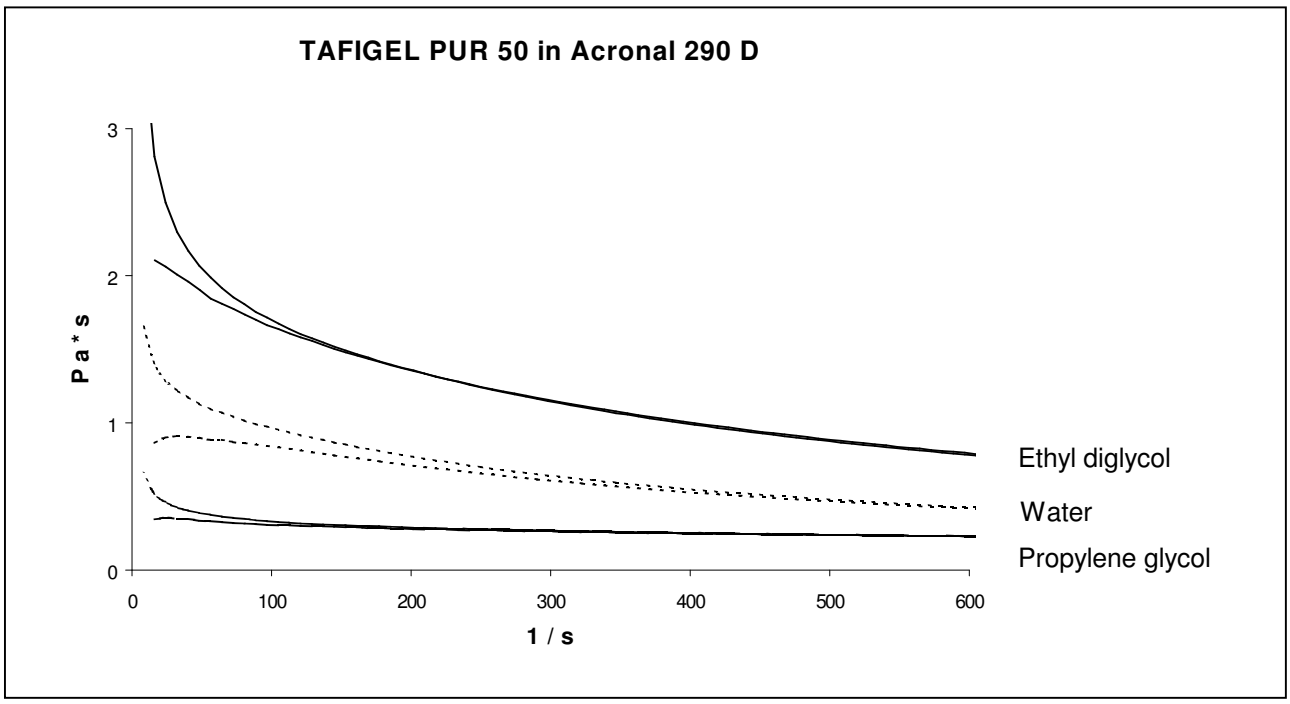


Figure 11: TAFIGEL PUR 50 in Acronal 290 D

5.7 Influence of wetting agents

Wetting agents show similar hydrophobic interactions and compete with polyurethane thickeners for the surfaces of emulsion particles. The addition of wetting agents usually decrease the viscosity by replacing thickener molecules on the emulsion particle surface. Thus the network is weakened. This influence is dependend on type and quantity of the wetting agent but also on the type of thickener. Generally the viscosity of systems with pseudoplastic rheology drops on addition of wetting agents. Figure 12 shows the influence of different types of wetting agents on the viscosity of a pseudoplastic thickener.

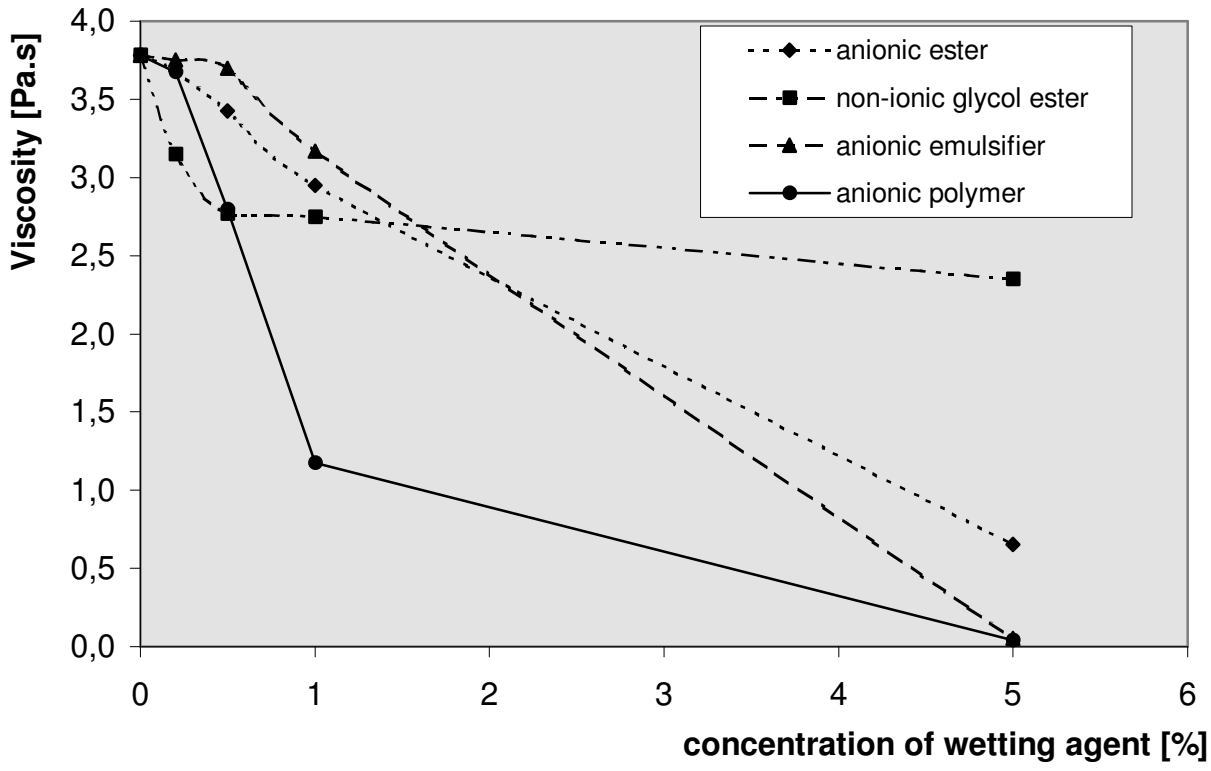


Figure 12: Influence of wetting agents on a pseudoplastic thickener

Figure 13 shows different behaviour of those wetting agents when added to a newtonian thickener. The anionic polymer decreases the viscosity, whereas the non-ionic glycol ester increases the viscosity. The anionic ester initially increases the viscosity but leads to a drop on higher levels.

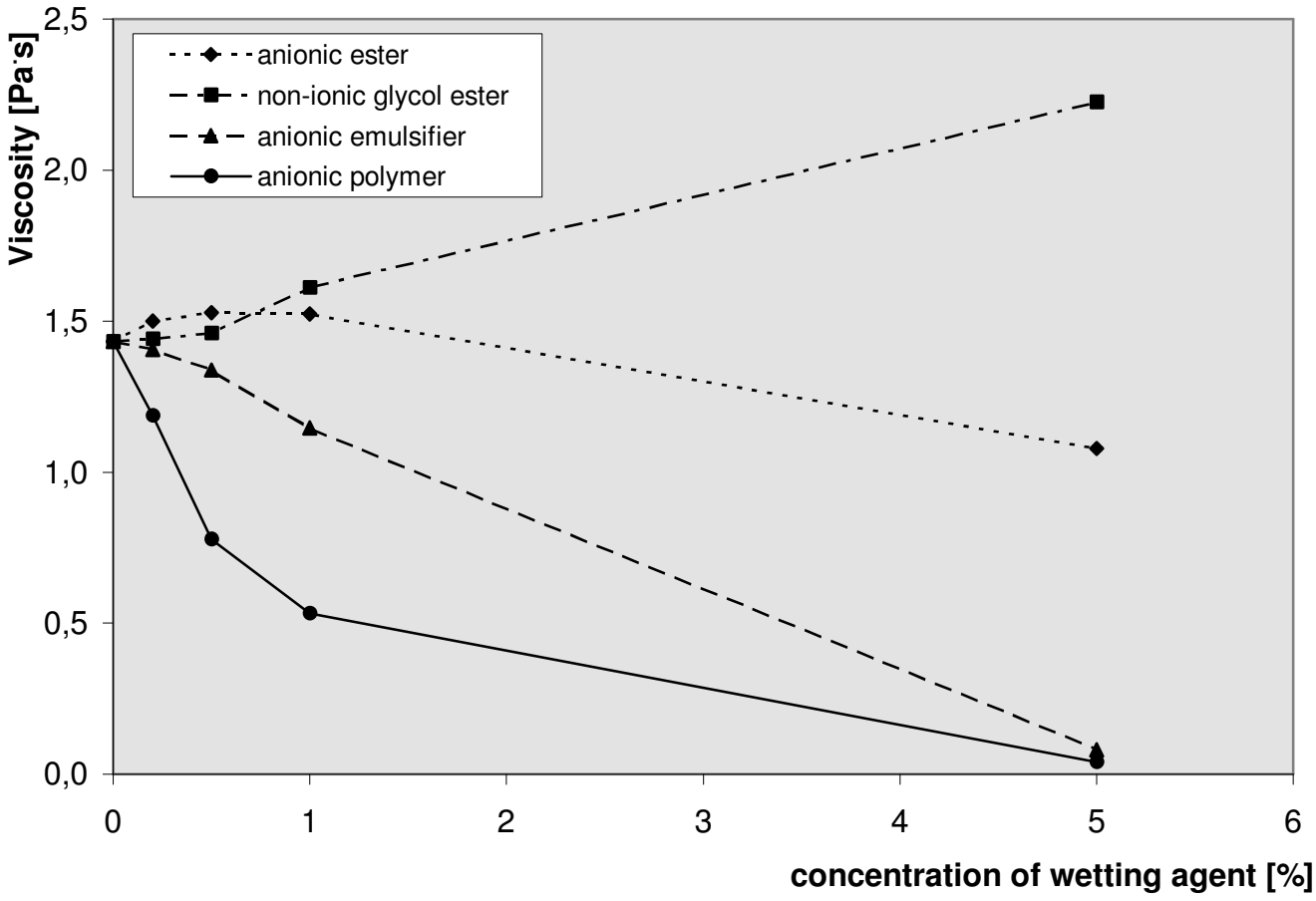


Figure 13: Influence of wetting agents on a newtonian thickener

5.8 Influence of solids

The addition of flatting agents like amorphous silica may influence the efficiency of polyurethane thickeners (Figure 14).

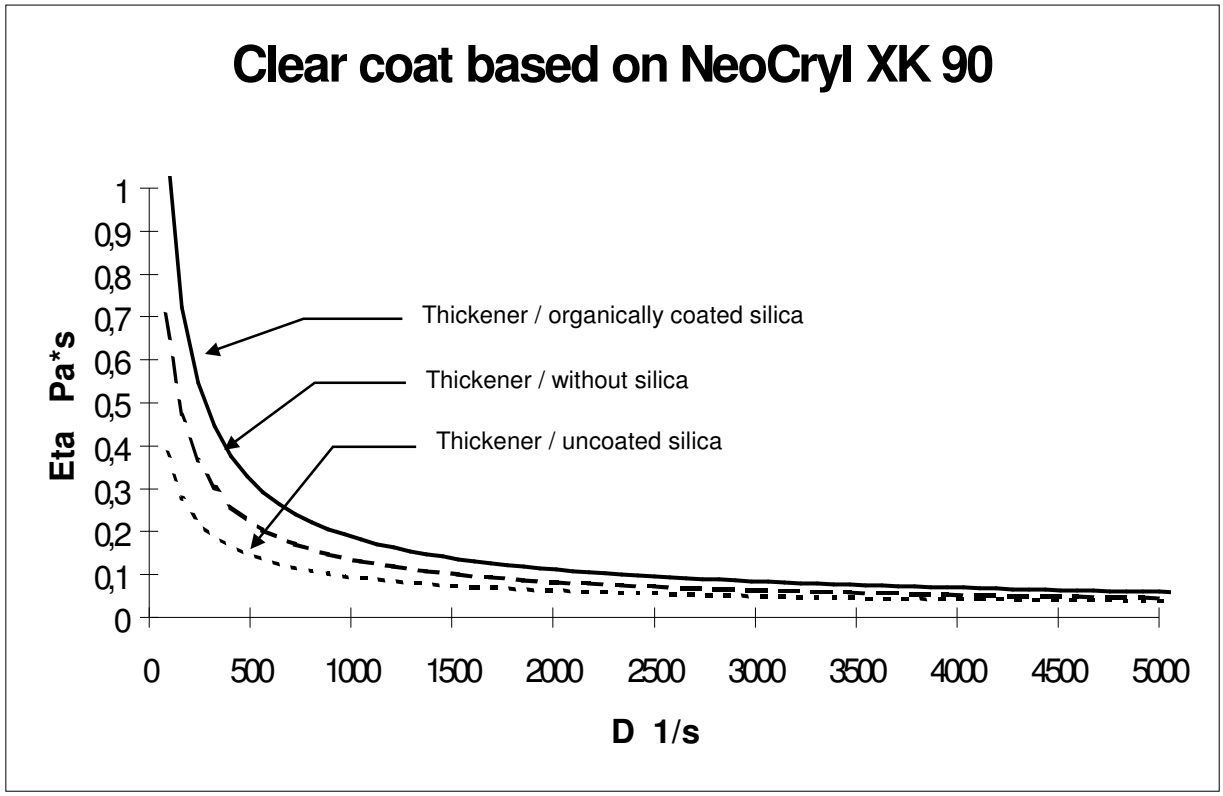


Figure 14: Influence of flattening agent on viscosity

The viscosity can increase in the presence of organically coated flattening agents like amorphous silica due to the increase of hydrophobic particles. Uncoated types of flattening agents generally decrease the viscosity.