Additives for Surface and Substrate

EDAPLAN® LA, METOLAT®, OMBRELUB®

Page

1. Basics

Substrate wetting – Levelling – Surface modifications
Defects in the surface constitution of coatings can be reduced in most cases on differences in the interfacial tension between coating and substrate.
These disturbances occur, when the liquid coating (in this case only water based coatings are regarded) are applied on a solid, non-absorbing substrate. In general, a waterborne coating has a higher surface tension than the substrate, on which it is applied. In this case the liquid tends to withdraw from the substrate instead of spreading on it, which would be necessary in order to obtain a homogeneous surface. A change in the surface tension of the coating is necessary to solve this problem. Table 1 gives an overview over surface tensions of common substrates, liquids and surfactants, which are used in paint, lacquer and adhesive industry.
Levelling defects can also be generated by effects, which are not based on differences in interfacial tension. These are rheological effects, application and solvent evaporation. In high pseudoplastic systems the fast build-up of structure prevents a uniform extension of the coating due to which a bad levelling is obtained. Application by brush or rough atomisation may also generate levelling defects. The evaporation of solvents can cause local surface tension differences, which create craters.
Levelling defects based on physical reasons cannot be cleared by levelling agents.

1.1 Surface tension

Values of surface tension for substrates, liquids and surfactants spread over a wide range. All aqueous coatings cause problems on substrates whose surface tension values are below the values of the coating.

Substrate	Surface tension [mN/m]	Liquids Solvents	Surface tension [mN/m]	Surfactants	Surface tension [mN/m]
Glass	37	Mercury	276	NPEO	35
phosphated steel	43 - 46	Water	72		
PVC	39 - 42	Diethylenglycol	49	Silicon surfactant	~ 30
Aluminium	~ 40	Xylene	32		
Polystyrene	36 - 42	Butylglycolether	30	Polyether-Siloxan-	
Zinced steel	35	Alkylbenzene	28 - 30	Copolymer	~ 20
Polyester	43	White Spirit	25 - 31	Anionic	
Polyethylene	32 - 39	Butylglycol	27	Fluorpolymer	~ 17
Polypropylene	28	Butylacetate	25		
Untreated Aluminium		Butanol	23		
	33 - 35	Organosiloxane	~ 22		
untreated steel	29	Isopropanol	22		
Polytetrafluorethylene	18	n-Octane	21		
		Dimethylsiloxan pure	21		
		Hexamethyldisiloxane	16		
		Isopentene	15		

Table 1: *Surface tensions of substrates, liquids and surfactants*

By addition of appropriate additives the values of surface tension can be lowered under the value of surface tension of the substrate. Highly efficient are siloxane and fluoro surfactants.

On a given surface a coating will spread or withdraw, depending on the surface tension values. In the case that the surface tension of the coating is higher than that of the substrate the coating will withdraw on the substrate in order to obtain the lowest possible common surface with the substrate. The angle that forms the liquid on the substrate is an indication for the ability of the liquid to spread on the substrate, respectively a possibility to determine the dimension for the surface tension relative to a reference. The angle ϑ_2 has values higher than 90°. A typical example for high surface tensions is mercury (see figure 1).

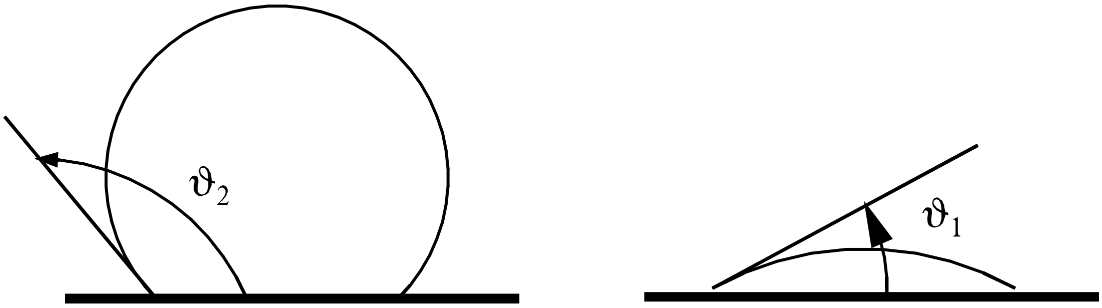


Figure 1: *Liquids with different surface tensions*

In the other case the surface tension of the liquid is smaller than that of the substrate and the liquid spreads on the substrate. In this case the angle ϑ_1 takes values $\vartheta_1 \leq 90°$.

In general the contact angle becomes smaller the better the wetting ability of the liquid. This means that the surface tension of the liquid has low values in comparison to the surface tension of the substrate.

1.2 Measurements of the surface tension

Surface tensions of liquids and solids can be determined by different methods. The surface tension of solids is determined with the contact angle method for which liquids with known spreading behaviour and surface tensions are taken as reference. For liquids there are two possibilities: either the contact angle method with a known substrate as reference or the ring method.
The contact angle method relies on a liquid or a substrate with known surface tension, depending whether the surface tension of a solid or a liquid shall be determined. On the substrate the liquid spreads or withdraws and by means of the resulting contact angle on the substrate the surface tension can be determined.

In the ring method (also known as method by *du Noüy*) an inert platinum ring is put into the liquid. The ring is torn out of the liquid measuring the resistance. The ring forms a lamellae that bursts when the surface tension has exceeded the limit. With the force which is necessary to tear out the ring and the diameter of the ring the surface tension of the liquid can be calculated.

1.3 Surface defects

Surface defects can be caused directly by extension (levelling) of the coating or by insufficient wetting of the substrate. In the applied film the following effects can be observed:

- crater
- orange peel
- fish eyes
- Bénard cells
- pinholes
- shrinkage
- sinking
- bad recoat ability
- brush drags (application effects), etc.

Most of the defects originate in differences in the interfacial tension. These defects can be removed by addition of appropriate additives. Brush drags however are caused due to the viscosity of the coating and have to be removed by changing the rheological properties of the coating.

1.4 Influences on levelling

The appearance of levelling defects depends not only from the differences in interfacial tension of substrate and coating but also from the following (physical) parameters:

- Viscosity of the film
- Open time
- Film thickness of the coating
- Evaporation of the solvent
- Drying time
- Method of application

Viscosity can influence levelling significantly. However, viscosity cannot be changed by levelling or surface additives (if these additives have no direct impact on viscosity or the thickener itself).
From a rheological point of view levelling takes place in the shear range of $1\ s^{-1}$. The viscosity value at this point decides over the levelling properties. In general, in comparison between a Newtonian and a pseudoplastic rheology modifier, levelling is better with a Newtonian type, as viscosity is lower in this shear range.
Thixotropic coatings level better, the higher the time period with which the system returns after shearing to its initial state.

The *film thickness* of a coating also influences levelling. In general, levelling is critical in thin layers of applied films. The thicker the film the better is levelling at the surface, given that the drying occurs in a homogeneous way. It is important to watch the dependence from open time as well.

The *drying time* influences the conditions of the surface due to solvent evaporation. The faster volatile components of the coating evaporate, the higher concentration differences are within the coating and the bigger are turbulences, which cause levelling defects.

1.5 Physical processes during drying

Film formation and drying of a coating occurs by evaporation of the volatile, liquid components and the fusion of binder molecules. In emulsion systems this unification of binder particles occurs with a strong volume contraction. In water reducible systems this contraction is quite smaller. The evaporation of liquid parts results in a permanent change in the surface tension of the coating because the combination of these compounds is altered constantly. At the same time viscosity is changed and due to the evaporation at the surface concentration differences are built up in the film.

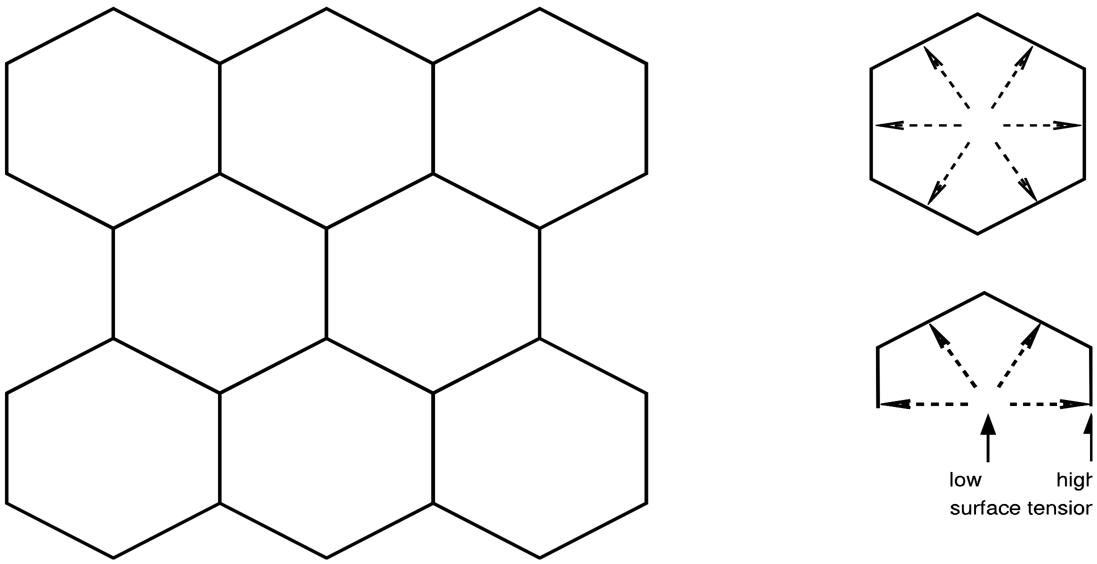


Figure 2: *Bénard cells (formation in the lacquer, from the top)*

These processes cause currents of solvents from deeper layers to the surface which results in turbulences in the coating, which on the other hand influence the surface properties.
The currents cause, that more light and volatile particles are transported to the surface whereas heavy particles due to differences in density and size sink to the bottom. Regions of sediments are formed in which more light particles are separated from more heavy ones, which can be observed in the formation of regular pattern on the surface: so called Bénard cells (figure 2). At the borders of these cells surface tension is high whereas in the middle of the area lower surface tensions are present.

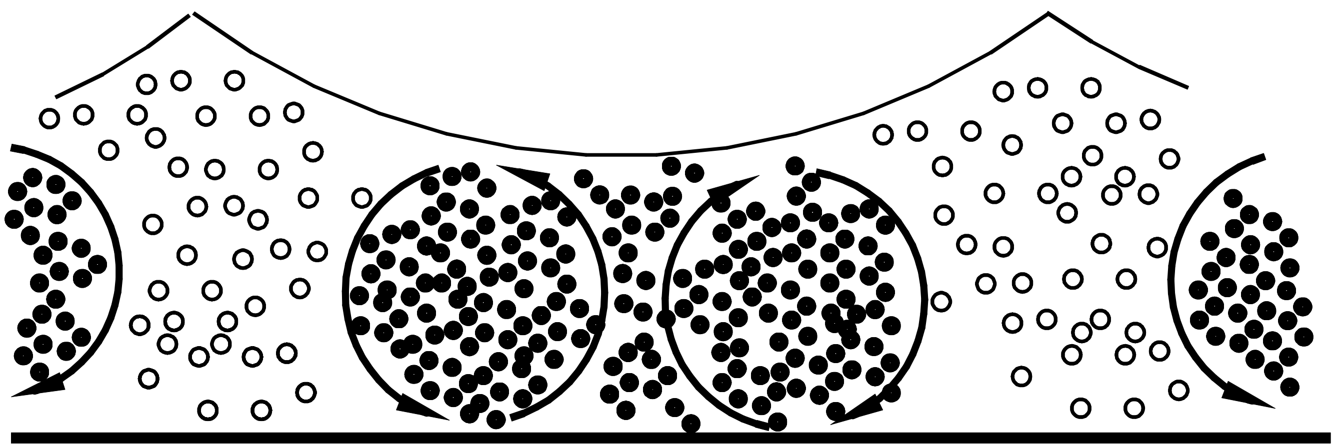


Figure 3: *changes in the tone due to formation of Bénard cells*

In addition to inhomogeneous conditions at the surface flotation effects can occur if pigments of different colours and different weight are present. A change in the tone occurs because the heavy pigments sedimentate in the drying period due to currents and turbulences. The lighter pigments swim up in the coating or form borders. This separation of pigments leads to the formation of cells in which the colour of the border is different from that in the including areas (figure 3).

In unpigmented systems or coatings with only one type of pigment currents are also caused which leave a structure on the surface. Mainly orange peel is observed as consequence.
Under extreme drying or evaporation conditions the surface of the drying film can even crack.

1.6 Prevention of surface defects

Levelling agents are able to cure or to avoid surface defects by taking an influence on the surface tension of the system. Generally, surface tension of the coating is lowered. This results in a better wetting of the substrate but levelling and surface agents are also able to keep the tension constant during drying. Due to this no differences in surface tension by the evaporation of the solvents results.
Other types of levelling agents does not influence the surface tension but just control the evaporation of solvents due to the fact that they have a controlled incompatibility due to which they rise to the surface. These kinds of additives block the coating surface against a too fast evaporation of volatile compounds but do not change (lower) the surface tension by themselves.
Wetting and dispersing agents can prevent surface defects in pigmented systems by avoiding inhomogeneous pigment distribution and stabilise pigments and protect them from flocculation
(⇨ EDAPLAN® - *Polymeric Dispersing Agents*).
Rheological additives can prevent surface defects in that way, that such thickeners are chosen, which do not rise viscosity in the region of shear forces where levelling occurs and where a build up of structure is not allowed
(⇨ TAFIGEL® PUR – *Rheology modifiers for aqueous systems*).

1.7 Surface modification: Smoothness, Scratch resistance, Water repellence

Regarding the film of a coating in first glance the binder is responsible for the properties and is chosen due to the desired properties for the final requirements. Especially hardness is determined by the binder type. Other properties like smoothness, scratch resistance, gloss, or water repellence can be influenced by additives.
Smoothness of the surface can be influenced by additives by which improvements regarding scratch and scrub resistance can be obtained. A smooth surface is not harder but gives less frictional resistance. That leads to a better gliding on the surface and less mechanical injuries (figure 4).

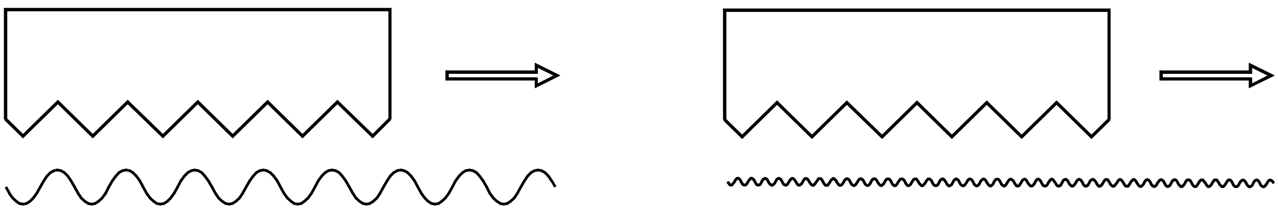


Figure 4: *Movement of a rough body relative to a surface*

If a rough structured body is moved over a rough surface slip resistance has to be overcome which is a force that is opposite orientated to the movement. The friction force is independent from the contact surface and only dependent from the structure of the surface. A smooth surface which shows macroscopically no waves or scars, shows in a microscopically scale up a certain roughness or surface structure (lotus effect, nano-particles).

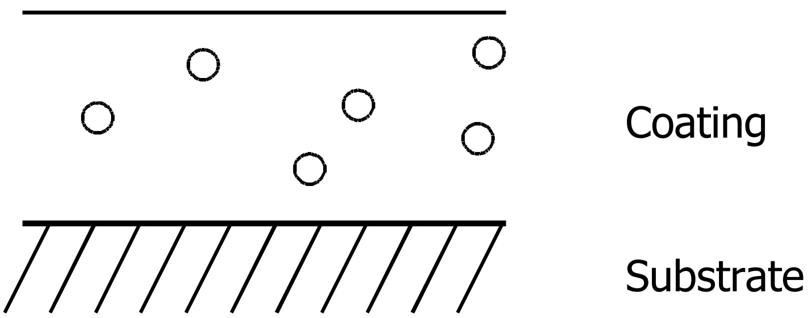
In order to increase slip of the surface special additives can be used which form a film in the surface which lets bodies glide on the surface. Especially modified polysiloxanes and waxes are used for this application.

Polysiloxanes are surface-active products which orientate on the surface of the film. With their hydrophobic ends they create a layer on the surface of the lacquer which equals irregularities. Polysiloxanes are active even in very low dosages. At higher rates they worsen adhesion and tend to stabilise foam.
(⇨ EDAPLAN® LA 411, EDAPLAN® LA 413)

Waxes (natural and synthetic) also form a layer on the lacquer surface which reduces gliding friction. They are more persistent as silicones and do not create problems at recoating. Waxes are applied as emulsions and the particle size determines the application range. A big particle size might reduce gloss. Waxes have to be applied in higher concentrations than polysiloxanes. Due to these quantities they increase water repellence of the film.
(⇨ OMBRELUB® 533)

1.8 Substrate wetting

As discussed already previously surface tension of an aqueous coating often has to be reduced in order to achieve spreading and a homogeneous surface of the coating.



$$\sigma_C \leq \sigma_S$$

A good substrate wetting of the coating is the requirement for a sufficient adhesion of the dry film. Generally, many wetting agents and solvents are able to reduce the surface tension of an aqueous coating under the value, which is relevant for a certain substrate. With this lower tension the coating spreads on the substrate.
Often, the consistency of the substrate is inhomogeneous and results in the formation of craters, which are formed due to local pollutions. Additionally, the evaporation of solvents can cause punctual changes in the surface tension, by which craters are formed. Other formulation ingredients, like defoamers for example, which are too incompatible in the medium, can also change the surface tension of the coating punctually and lead to craters in the applied film. The defoamer has to be chosen carefully and has to be adapted to the special requirements (⇨ AGITAN® - Defoamers).
Surfactants based on polysiloxanes and especially fluoro based surfactants and special wetting agents remove local differences in surface tension or wet the substrate surface by which the adhesion is improved.
(⇨METOLAT® 285, METOLAT® 288)

2. Effect of additives

2.1 Silicone additives (organically modified polysiloxanes)

The most commonly used levelling agents are modified organo polysiloxanes. Simple silicone compounds do not reduce surface tension sufficiently, e.g. on low energetic surfaces like plastics. Polyether modified siloxanes of low molecular weight and surfactant like structure, however, lead to a strong reduction of surface tension. Smoothness of the surface is improved and scratch and blocking resistance is increased. In higher dosages silicone additives may reduce adhesion and tend to foam. Therefore they should be used in lower concentrations.
(⇨ EDAPLAN® LA 411, EDAPLAN® LA 413)

2.2 Acrylic based additives

Acrylate additives do not have a pronounced surfactant like structure and do not reduce surface tension. Due to controlled incompatibility they migrate to the surface where they are accumulated.
Acrylic levelling agents minimise especially the waves on the surface of the finished coating. They do not prevent formation of craters because for their prevention the surface tension has to be lowered. Acrylates do not show negative effects on the adhesion after recoating. In epoxy systems they can show additional deaerating effects. They are used in higher concentrations than silicone levelling agents but excess of acrylic levelling agents leads to sticky films.
(⇨EDAPLAN® LA 402, EDAPLAN® LA 403)

2.3 Special levelling agents

Apart from polysiloxanes and acrylates other additives based on different chemical nature than the ones mentioned above can be used, e.g. fluoro surfactants, special esters. They can be used if they reduce the surface tension or migrate to the surface and control the evaporation of volatile coatings compounds.
(⇨ EDAPLAN® LA 451)

2.4 Wax additives (Water repellence)

Waxes and wax emulsions based on natural or synthetic waxes are used for the protection of the surface. They do not influence neither surface tension nor prevent levelling defects. Waxes improve smoothness of the surface and increase scratch resistance and water repellence.
Wax additives can also influence rheology and lead to a more homogeneous distribution of solid particles in the liquid phase. This is desired especially for aluminium particles in metallic lacquers and matting agents in satinated systems.
Higher scratch resistance and better smoothness of the surface is obtained with polytetrafluoroethylene- and polyethylene waxes. Paraffinic waxes obtain a better water repellence.
(⇨ OMBRELUB® 533)

3. Polysiloxane levelling agents: EDAPLAN® LA 411 EDAPLAN® LA 413

	EDAPLAN® LA 411	EDAPLAN® LA 413
Composition	modified Siloxane glycol-Copolymer	modified Organo polysiloxane
Solubility	soluble in acetone, white spirit, alcohol; dispersible in water	soluble in non polar and polar solvents, fairly soluble in water
Surface tension		
pure product	approx. 22.6mN/m	approx. 23.3 mN/m
In aqueous solution	0.1%: approx. 33.1 mN/m 1.0%: approx. 29.3 mN/m	0.1%: approx. 38.1 mN/m 0.5%: approx. 35.1 mN/m
Flash point	approx. 80°C	above 65°C
Dosage	0.1 to 0.5% calculated on total of the formulation	0.05 to 0.15% calculated on total of the formulation
Characteristics	• improves slip • suitable also for solvent based systems	• stable to hydrolysis • deaerating properties
Application	• waterborne lacquers • water reducible resins • powder coatings	• water and solvent borne lacquers • transparent systems • parquet lacquers based on PU-acrylic resins

4. Acrylate levelling agents: EDAPLAN® LA 402 EDAPLAN® LA 403

	EDAPLAN® LA 402	EDAPLAN® LA 403
Composition	silicone free acrylic polymer, dissolved in butylglycol	silicone free acrylic polymer, in combination with surfactants. Anionic.
Soluble in	after neutralisation soluble in water	soluble in water
Surface tension	approx. 35,6 mN/m	approx. 40 mN/m
Neutralisation	100 g EDAPLAN LA 402 need 3,6 to 4,2 g NaOH or 12,5 to 15,0 g NH_4OH (25%) acid number: approx. 55 mg KOH/g	pre-neutralised
Characteristics	• improves gloss • reduces haze gloss • silicone free • prevents surface defects • does not influence water sensitivity	• improves gloss • reduces haze gloss • silicone free • compatible with all commonly used binder types • prevents surface defects • does not influence water sensitivity
Properties	• provides deaerating properties.	• especially for chemical curing and two pack reaction systems • provides deaerating properties
Application	• for all aqueous coatings systems • printing inks • and overprint varnishes	• for all aqueous coatings systems • printing inks • and overprint varnishes
Dosage	0.5 to 3.0 %	1.0 to 2.0%

5. Special levelling agents: EDAPLAN® LA 451

	EDAPLAN® LA 451
Composition	silicone free ester in an ethanol/water mixture
Solubility	in water emulsifiable, can be diluted with 10 - 20% water in 1,2-propylene glycol dilutable up to a 1:1 ratio.
Surface tension	approx. 27 mN/m
Properties	equalises surface tension in aqueous systems no problems with recoatability due to silicone free formulation
Characteristics	levelling agent for wide application possibilities, silicone free and not foam creating
Advantages	• improvement of gloss and reduction of haze • prevention of surface defects • improvement of substrate wetting • no tendency of foam formation
Applications	• lacquers and industrial paints • wood and parquet lacquers • automotive OEM and repair • printing inks, overprint varnishes
Dosage	0.1 - 1.0 %

6. Substrate wetting additives: METOLAT® 285 METOLAT® 288

	METOLAT® 285	METOLAT® 288
Composition	water-soluble, anionic ester, silicone free	anionic ester, silicone free
Solubility	soluble in water	easily emulsifiable in water
Surface tension	approx. 28 mN/m	approx. 30 mN/m
Properties	wetting agent with good substrate wetting properties emulsifier for defoamers, which are difficult to incorporate	wetting agent with good substrate wetting properties and low foam formation tendency
Characteristics	• wetting agent for alkaline systems • improves also incorporation of defoamers which are difficult to emulsify • prevents defects which are caused by over dosage of defoamers	• improves wetting of surfaces, especially PE, PP and coated aluminium sheets • improves gloss and colour strength in overprint varnishes
Applications	• all paints, lacquers, varnishes, adhesives and inks, where defoamer has to get incorporated	• overprint varnishes • container coatings • printing inks • wood lacquers • adhesives
Dosages	0.1 to 0.5% as substrate wetting agent (10 to 30% calculated on defoamer quantity for defoamer incorporation)	0.1 to 2.0% calculated on total of the formulation

7. Wetting agents: METOLAT® 355 METOLAT® 388

	METOLAT® 355	METOLAT® 388
Composition	Polyamine ethylene oxide condensate, non-ionic, silicone free	Blend of polyglycol esters, silicone free
Solubility	soluble in water	easily emulsifiable in water, soluble in most common solvents
Surface tension	approx. 40 mN/m	approx. 33 mN/m
Properties	wetting agent with low foaming tendency	wetting agent for pigment and substrate wetting
Characteristics	• high stability to alkaline and acid systems • good compatibility due to non-ionic character	• biodegradable product • especially for use in environmentally safe systems
Applications	• wetting agent for aqueous systems • for wetting of organic pigments • improves compatibility and levelling in emulsion paints and lacquers	• wetting of organic pigments • improves pigment dispersion in emulsion paints • prevents flocculation of particles caused by emulsifier migration and mechanical or thermal shocks
Dosages	0.1 to 0.5%	0.1 to 0.3% calculated on total of the formulation

8. Water repellence agents: OMBRELUB® 533
Release agent: OMBRELUB® RA

	OMBRELUB® RA	OMBRELUB® 533
Composition	combination of liquid hydrocarbons and surface active substances	stable emulsion of finely dispersed calcium stearate; non-ionic
Solubility	easily emulsifiable in water	miscible in water at any ratio
Properties	release agent for strippable coatings	laminar structure of calcium stearate BgVV and FDA conformity
Characteristics	• for all common substrates • no migration • no colour change • efficient after storage at elevated temperatures	• improves slip in printing inks • increases waterproof properties • protection against humidity • reduces water uptake in prefabricated concrete parts • turns pores of concrete hydrophobic
Applications	• strippable paints • transport protection coatings • spray booth coatings • hobby paints	• printing inks and overprint varnishes • wood coatings • concrete surfaces
Dosage	in general 1 – 2 % calculated on total of the formulation	0.5 – 2% in inks and other coatings 2% in cement and concrete calculated on cement

9. Emulsifiers: METOLAT® TH 75 LEUKONÖL® LBA 2

	METOLAT® TH 75	LEUKONÖL® LBA 2
Composition	sulphated fish oil, Na-NH_4-salt	sulphated castor oil
Solubility	easily emulsifiable in water	miscible in water at any ratio
Surface tension	approx. 36 mN/m	approx. 41 mN/m
Properties	anionic emulsifier	emulsifier for aqueous systems, especially for emulsion polymers
Characteristics	emulsifier with low tendency to foam formation	in alkaline solutions clearly soluble up to pH 13
Application	emulsification of mineral and vegetable oils in water	production of polymer emulsions wetting agent for alkaline solutions
Dosage	10 - 50% calculated on the compound to be emulsified, exact quantity has to be determined in previous trials and depends on the degree of emulsification as well as the raw materials.	has to be determined in previous trials