



The application and properties of high tech aqueous top coats

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There is an increasing interest in water-based top coat systems in the leather industry. Traditionally, NC and organic CAB lacquers have been the product groups requiring the greatest amount of organic solvents and are therefore the primary target for solvent reduction or total elimination.

During the last few years a strong worldwide shift from solvent to water-based systems has taken place. The first aqueous topcoats for the leather industry were introduced at the beginning of the 1980s^(Legend 1). Over the following years this range continuously expanded for a wide range of leather articles, starting at fashionable shoe articles, and ending at high performance top coat systems for car upholstery and sport shoe leathers.

The most important parts in a high performance coat system are the polymer binders within the individual glossy and dulling components. However, there are both organic-based top coat systems and water-based top coat systems, the basic differences being:

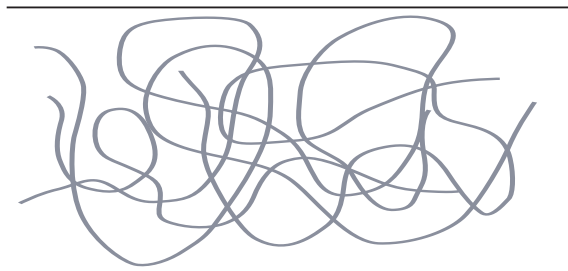
- the organic solvent content
- flow out
- film formation
- drying conditions

LACQUER BASED TOP COAT SYSTEMS

Lacquers are polymers in solution, so the polymer chains are fully mobile in the solvent medium. Free-moving polymer chains will form a well-entangled film during the drying process as illustrated in *Figure 1*.

The film formation of organic-based top coats is further enhanced by the addition of plasticisers being added to keep the polymer soft. Another characteristic of NC and CAB lacquers is the low surface tension of organic solvents compared with water.

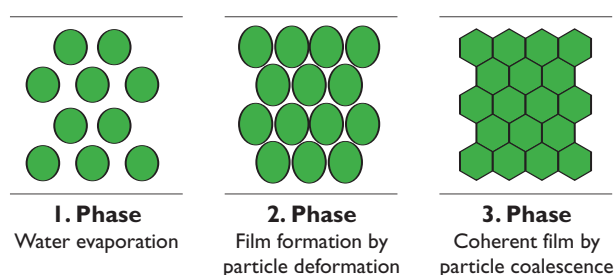
Figure 1: Film formation of organic top coats



AQUEOUS TOP COAT SYSTEMS

Aqueous top coat systems are completely different from lacquer solutions, as they comprise discrete particles dispersed in water. Each particle contains a number of entangled polymer chains. During the drying of the top coat, the water evaporates and the particles are packed together to form a honeycomb structure as illustrated in *Figure 2*.

Figure 2: Film formation of waterbased top coat systems



How well the particles are packed together and the polymer chain entanglement will directly affect the performance of the top coat.

Composition of a water-based top coat system

In general, a water-based top coat system consists of several components:

- Dull resins
- Gloss resins
- Thickener
- Levelling/wetting agent
- Feel agents
- Defoaming agents
- Crosslinker

DULLING AND GLOSSY TOP COAT RESINS

These are mainly polyurethane or acrylic dispersions with selected dulling agents and auxiliaries. These can provide different degree of hardness, gloss, flexibility and other relevant physical properties to cover the needs of modern leather finishing.

THICKENING AGENTS

Thickening agents are very important for the application of water-based top coat systems. There is a wide range of these products to cover the different uses, including:



- adjustment of the viscosity
- ensuring consistency of viscosity during application
- improvement of levelling
- thixotropic behavior

LEVELLING AGENTS

These products level the flow and reduce the surface tension, so are very important for application purposes. In the past, solvents were used for this purpose in water-based systems, however, high performance solvent-free levelling agents are now used. These improve the flow and also support the penetration of the top coat or the base coat. An example of performance is given in *Figure 3*.

Figure 3: Surface tension of solvents

Solvents	Surface tension (mN/m)
Melio LV-03 (leveller)	23
Water	73
Ethyleneglycol	48
MEK	25
Butanol	25
Xylene	30
Silicone oil	23
Ethylglycol	28
Toluene	28

FEEL AGENTS

Feel agents are used to adjust the handle and the physical properties of the top coat. There are many different agents that can be used alone or in combination to adjust the feel and/or improve selected physical properties, such as the abrasion fastness. The tactile properties can be described as dry, waxy, oily, greasy, slippery, silky, and can be achieved to varying degrees.

DEFOAMING AGENTS

These agents are especially useful for roller coater applications, but are also suitable in spray coats.

CROSSLINKERS

These are reactive components which crosslink the polymer particles and vastly increase the fastness properties. Most of the high performance top coat systems require a crosslinker to maximise the physical performance. These cross linkers react with very specific groups in the finish as shown in *Figure 4*.

The molecular structure of the polymers is thus enhanced by crosslinking, and these products also react with hydrophilic groups of other additives and feel agents. Main improvements are found in wet fastness and abrasion resistance.

Crosslinking agents can also improve the intercoat adhesion by linking:

- the top coat with the base coat
- the base coat with crust or preground
- the preground with the crust

If used in pregrounds and base coats, there is an increase in:

- the molecular weight of the polymers



- the hardness throughout the finish
- the physical properties
- blocking of hydrophilic groups
- the intercoat adhesion.

Figure 4: Crosslinkers

CROSSLINKER			
chem. base	reacts with	reactivity	pot life
Aziridine	-COOH; -NH; -OH		<1d
Isocyanate	-NH; -OH; -COOH; -NH-CO-NH		<8h
Epoxy	-NH; -OH; -COOH		<2-3d
Carbodiimide	-COOH		<2d

Types of crosslinking agents

There are four main crosslinker types for water-based systems:

AZIRIDINE

This is the most powerful and easy to use crosslinker, because it is less temperature dependent compared with the alternatives. The product can be used in both base and top coats. The yellowing resistance against heat and light is, however, limited.

ISOCYANATE

New generation isocyanates are very easy to disperse into the prepared aqueous mixes for application. These have a high reactivity and can be used in base and top coats. There is high resistance to yellowing under conditions of heat and light.

CARBODIIMIDE

This is the most selective type of product as they only react with carboxylic groups. Compared with aziridine and diisocyanate crosslinkers, they exhibit a medium high reactivity, and are mainly used in combination with isocyanates to accelerate their reaction speed.

EPOXY

These products are less effective than aziridine and diisocyanate crosslinkers, hence have a longer pot life in prepared application mixes. They are mainly used in base coats and have a limited yellowing resistance against heat and light.

Parameters for using crosslinkers

QUANTITY

The quantity of crosslinking agent is very important for its application. For each top coat system there is an optimum amount and type, depending on the quantity of polymer used, the functional groups, and on the type and quantity of auxiliaries in the formulation. Excess can result in a lower wet rub resistance, as shown in *Figure 5*, low film flexibility, and in intercoat adhesion problems.

DRYING TEMPERATURE

To start the reaction between the crosslinker and the polymers, some temperature activation is needed. An increase of approximately 10°C will double the reaction rate, so, if the drying temperature is raised from 80°C to 100°C, the reaction rate increases four times. ➤



Figure 5: Crosslinker vs. Concentration

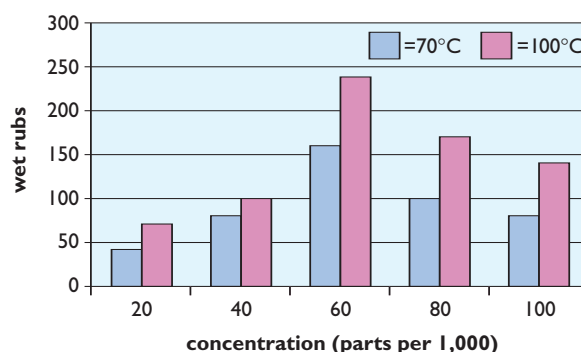


Figure 6: Aqualen System - application amounts guideline

Dry quantity		
Car upholstery leather	0.8 - 2.4 g/sqf	1-2 spray coats
Furniture upholstery	0.5 - 1 g/sqf	1 spray coat
Shoe upper leather	0.4 - 0.6 g/sqf	1 spray coat
Aqueous patent leather imitation	2.5 - 3.5 g/sqf	1-2 reverse roller coater

The application of aqueous top coats

In general, organic lacquers have better flow-out properties and, with regard to thin coats, provide better wet rub fastness than purely water-based top coat systems.

With aqueous top coat, the quantity applied plays a decisive role in both the levelling and fastness properties. A guideline for the quantities required by different articles is given in *Figure 6*.

Drying conditions for aqueous top coats

The properties for the final top coat are very dependent upon the drying conditions. This is because aqueous top coats require more energy for evaporation than conventional solvent containing NC or CAB lacquers, as shown in *Figures 7a & 7b*.

However, the heat used when drying has several functions, so that in addition to driving off water and the other volatile components, the top coat polymer particles are softened. This

Figure 7a: Heats of evaporation for top coat systems

Waterbased top coat system	2100 J/g
CAB lacquer emulsion	900 J/g
CAB lacquer emulsion/polyurethane Dispersion 1/1	1500 J/g
CAB lacquer	420 J/g

Figure 7b: Boiling points and heats of evaporation of solvents

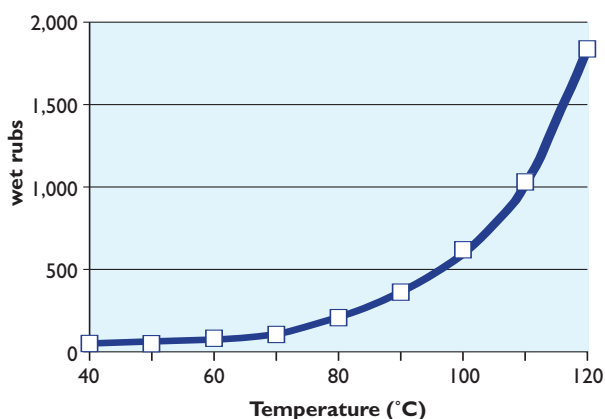
Components	Boiling point	Heat of evaporation
Water	100°C	2480 J/g
Ethanol	78°C	870 J/g
Cyclohexanone	156°C	460 J/g
Toluene	110°C	360 J/g
Methylethylketone	80°C	468 J/g
Butylacetate	126°C	309 J/g



softening allows the particles to deform upon drying and merge together for an optimal film formation; the water content within the film at this stage acting as a plasticiser. It is, however, important to ensure that no moisture remains in the final film otherwise there will be problems with tackiness during embossing and during piling.

Another important function of heat is that it accelerates the crosslinking of the top coat, so for all of these different reasons the drying temperature can strongly influence the final optic and fastness properties of the top coats. As an example, *Figure 8* shows the influence of temperature on the wet rub resistance when the drying time remains constant.

Figure 8: Drying conditions of a waterbased top coat system



General rules for drying

The role of drying is very important in film formation. These can be generalised:

- The required drying temperature is between 90-110°C. Minimum drying time 90 sec.
- It is recommended to run a temperature profile including a peak temperature over 100°C.
- The surface temperature should reach 90°C in order to activate the crosslinkers. The lower the temperature, the longer is the reaction time.
- The first stage of the drying should not be too hot. This is to avoid a film formation occurring only on the surface of the finish layer. A lower entrance temperature also allows a better flow-out of the top coat.
- All incoming air should be filtered.
- A combination of steam heaters and IR heaters can provide good results.

The viscosity

The viscosity of the top coat mix is very important. This directly influences the levelling behaviour and therefore both physical and optic properties. For example, the appearance of a 'white break' in the valleys of embossed leathers with a high degree of dullness, is because the dulled top coat was applied with too low viscosity. When conventional spraying techniques are used, the ideal viscosity for a top coat (Aqualen) is about 17-23 sec Ford Cup 4. In case of high application quantities on already embossed leathers, and/or when using HVLP, airless or roller coater applications, the ideal viscosity will be higher - in some cases perhaps 40-50 sec. Ford Cup 4. ➤



Figure 9: Topcoats for different leather articles

Examples are given of top coat formulations for different types of leathers. It is noted that due to different requirements of car manufactures in terms of appearance, handle and physical properties, three basic examples are given.

1. Car upholstery (Asian, European, American market)

Products	Asian	European	American
Neosan 2000 pigments	0-30	0-30	0-30
Water	200	200	200
Aqualen Top D-2018 ⁽¹⁾	200-300	200-400	200-300
Aqualen Top DP-2055 ⁽¹⁾	0-100	0-200	-
Aqualen Top D-2017 ⁽¹⁾	or 0-100	or 0-100	100-200
Aqualen Top 2007.A ⁽¹⁾	-	50-150	-
Aqualen Top 2003.A ⁽¹⁾	100-150	-	50-150
Aqualen Top 2006.B ⁽¹⁾	-	50-150	50-150
Melio 09-L-13 ⁽¹⁾	50-100	-	-
Melio LV-03 ⁽⁴⁾	30	30	30
Melio WF-5233 or Melio WF-5226 conc. ⁽³⁾	30-60	5-30	30-60
Melio WF-5227 ⁽³⁾	0-20	0-30	0-20
Aqualen IVV-80.A ⁽⁵⁾	60-80	50-60	60-80
Aqualen Paste VN/VS ⁽²⁾	X	X	X
Application	2 x spray (40 g/m ² wet) viscosity 25" FC4	2 x spray (30 g/m ² wet in total) viscosity 20" FC4	2 x spray (each 40 g/m ² wet) viscosity 25" FC4

2. Other leather types

Products	Furniture Upholstery	White Sport Shoe Upper Leather	Shoe Upper, Full grain, Glazed Imitation	Fancy Leather, High Gloss	Aqueous Patent Leather Imitation
Neosan 2000 pigments	-	50	0-50	-	-
Supronil HK dyes	-	-	0-10	-	5
Aqualen Top DC-2040.A ^(1A)	600	-	-	-	-
Aqualen Top GC-2030 ^(1A)	-	-	600	-	-
Aqualen Top GC-2031 ^(1A)	-	-	-	350-500	-
Aqualen Top D-2018 ⁽¹⁾	-	300	-	-	-
Aqualen Top 2007.A ⁽¹⁾	-	200	-	-	-
Water	400	240	375-400	700-500	50
Melio WF-5233 ⁽³⁾	-	20	-	-	-
Aqualen Top LN.A ⁽¹⁾	-	-	-	-	1000
Melio Top 239 or Melio Top 297 ⁽⁶⁾	-	-	-	-	0-50
Melio WF-5230 ⁽³⁾	-	-	-	-	50
Aqualen AKU ⁽⁵⁾	10-12	-	12	8-10	15-20
Aqualen IVV-80.A ⁽⁵⁾	or 50-60	50	-	or 35-50	-
Aqualen Paste LN.A ⁽²⁾	-	-	-	-	X
Aqualen Paste VN/VS ⁽²⁾	X	X	-	-	-
Application	1 x spray (30 g/m ² wet) viscosity 20" FC4	1 x spray (30 g/m ² wet) viscosity 25-30" FC4	1-2 x spray, plate rotative 140°C/20 bar viscosity 17-18" FC4	1-2 x spray, plate rotative 120°C/20 bar viscosity 7-10" FC4	2 x reverse roller coater each 40-50 g/m ² , plate rotative 120°C/50 bar viscosity 22-25" FC4

Products in Figure 9 are registered names by Clariant GmbH.

⁽¹⁾ = Topcoat Binders with special properties, dull or glossy

^(1A) = Compacted Topcoat with special properties, dull or glossy

⁽²⁾ = Thickening agents

⁽³⁾ = Feel agents

⁽⁴⁾ = Levelling agents

⁽⁵⁾ = Crosslinking agents

⁽⁶⁾ = Casein, glossy

Legend

1. Aqualen® System by Clariant (Deutschland) GmbH