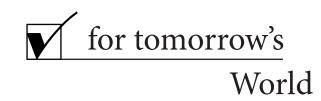


CODIS[™] 95 & CODIS[™] BIO ADDSPERSE[™] PH

Neutralising Agents



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1. Introduction

Amines are used in emulsion polymerisation to provide mechanical stability of resultant dispersions and also in coatings manufacture to assist with pigment dispersion, grind stability if dispersing pigments into polymer dispersion and also pH buffering of dispersion coatings.

Ammonia is the most commonly used amine, being low cost, but is highly odorous and has high volatility resulting in pH instability. To overcome these disadvantages formulators have looked at successfully incorporating various alkanol-amines. In addition to lower volatility and lower odour, these alkanol-amines also allow superior corrosion resistance, VOC reduction in formulation, excellent pH buffering and very good pigment dispersion properties.

After application of the wet coating, the pH-adjusting agent MUST either, at least partially, evaporate from the film in order to promote the coalescence of the resin binder and to avoid poor early water resistance or become completely inert in the resulting coating film.

ADDAPT® Chemicals BV now markets CODIS™ 95, a proprietary blend of alkanol-amines with an active content of 90%. This is an almost colourless liquid with a low viscosity, that remains liquid at temperatures below -10°C and withstands > 5 freeze/thaw cycles at -15°C. It is an excellent pH-buffer with emulsifying properties.

Additionally, ADDAPT® Chemicals BV markets CODIS™ BIO, a multifunctional neutralising agent for Ecolabel certified paints. It enhances compatibility with pigments, wetting and flash rust inhibition. It is based on renewable components, VOC-free and without hazardous labelling.

ADDSPERSE™ PH contains a proprietary blend of alkanol-amines in water. It provides very effective pH control for low odour systems. It has minimal contribution to VOC.

2. Typical properties

	CODIS™ 95	CODIS™ BIO	ADDSPERSE™ PH
Appearance	Clear, colourless liquid	Clear, colourless liquid	Clear, colourless liquid
Colour (APHA)	≤15	≤100	-
Active content	~90%	~50%	~68%
Water content	~10%	~50%	~32%
Freezing point	< -10°C	< -10°C	< -10°C
Freeze/thaw stability	> 5 cycles at -15°C	> 5 cycles at -15°C	-
pH (1% aqueous solution, 25 °C)	10 - 12	9 - 10	11 - 12
Density at 25 °C	1.05 - 1.10 g/cm ³	1.14 - 1.17 g/cm ³	1.12 - 1.16 g/cm ³

CODIS™ 95 and CODIS™ BIO are proprietary blends containing alkanol amines in water. All constituents are EINECS, TSCA, ENCS, AICS, DSL, ECL and PICCS registered.

3. Performance benefits

CODIS™ BIO
Very efficient neutralising agent
Improves tinting strength
Improves storage stability
Improves open-time
In-can corrosion protection (flash rust)
No odour
• No VOC
Readily biodegradable
Label-free

ADDSPERSE™ PH

- Very efficient neutralising agent
- Strong buffering action, stabilisation of pH over a long period of time
- · Exhibits high gloss, good water resistance and anti-corrosion properties
- · Low tendency towards yellowing
- Low VOC low to medium volatility
- Especially suitable for VA/VeoVa-based systems
- Low odour

4. Performance - Water-based systems

4.1 Amine comparison - primary/secondary/tertiary

Amine	Composition	Comments
CODIS™ 95	Blend of alkanol-amines in water	No secondary amines
CODIS™ BIO	Proprietary blend	Tertiary amines
ADDSPERSE™ PH	Blend of alkanol-amines in water	No secondary amines
AMP 95	2-amino-2-methyl-1-propanol	Primary amine - < 7% sec. amine
ADVANTEX	2-(n-butylamino)ethanol	Secondary amine
Ammonia	NH ₃	Primary amine

4.2 Yellowing

To test for yellowing, CODIS™ 95 and CODIS™ BIO were added to a beaker glass and exposed to air at room temperature. No change in colour was observed over a period of 2 months.

Furthermore, CODIS™ 95 and CODIS™ BIO were added at a level of 0.5% to neat styrene/acrylic, acrylic, VA/acrylic and VA/VeoVa emulsions. Samples were stored at 50°C for 1 month. Again no discernible yellowing was observed.

4.3 Cobalt leaching

The leaching of cobalt from tungsten-carbide tools can shorten tool life and the presence of cobalt in the used fluid can lead to dermatitis and/or inhalation problems for exposed workers as well as cause problems in wastewater disposal. CODIS™ 95 exhibits minimal cobalt leaching.

4.4 Nitrosamine formation

Nitrosamines and especially *N-nitrosamines* are considered to be very *carcinogenic*.

Secondary (alkanol)-amines are the most potent to form N-nitrosamines. These N-nitrosamines are readily formed by the reaction of secondary (alkanol)-amines with nitrites or nitrogen oxides.

Germany instituted regulations in the 1990s that prohibited the use of secondary amines in metalworking fluids. Both primary and tertiary amines can be used in metalworking formulations and metal primers with little risk of nitrosamine build-up.

4.5 Wet Adhesion – Early water resistance

Since the introduction of AMP 95, other alkanol-amines have entered the marketplace; all claiming to have performance benefits. These alkanol-amines, along with ammonia, were assessed for film resistance properties in Revacryl DP5530 (ex-Synthomer).

4.5.1 Amines evaluated

Amine	Composition	Comments
CODIS™ 95	Blend of alkanol-amines in water	Low odour, medium volatility
CODIS™ BIO	Proprietary formulation in water	No odour, non-volatile
AMP 95	2-amino-2-methyl-1-propanol	Low odour, slow volatility
ADVANTEX	2-(n-butylamino)ethanol	Low odour, very slow volatility
Ammonia	NH ₃	Strong odour, fast volatility

4.5.2 Experimental

Each amine was added at 0.2% addition level to neat Revacryl DP5530 (ex-Synthomer). Films were then applied at 100 microns wet film thickness onto degreased cold rolled steel panels. Panels were dried for 15 minutes at 60°C then 16 hours at room temperature. Panels were then soaked in tap water for 48 hours. On removal from water, panels were patted dry and a 'cross hatch adhesive tape pull-off' test performed.

4.5.3 Results

Amine	Wet adhesion (% film removed)	
CODIS™ 95	0	
AMP 95	100	
ADVANTEX	60	
Ammonia	0	

4.5.4 Discussion

It is evident that the amine choice has a major effect on the wet adhesion of the polymer film onto cold rolled steel in this instance. Excellent results were obtained with ammonia and CODIS™ 95. It is believed this is due to the volatility of each amine under test, with lower volatility amines still being present in the film and imparting water sensitivity, in combination with a function of neutralisation of carboxylic groups present in the polymer.

5. Performance - Solvent-based systems

The ability to incorporate high levels of water in solvent-based alkyd paints is shown in the following section where the performance of CODIS™ 95 is compared with a well-known competitive product.

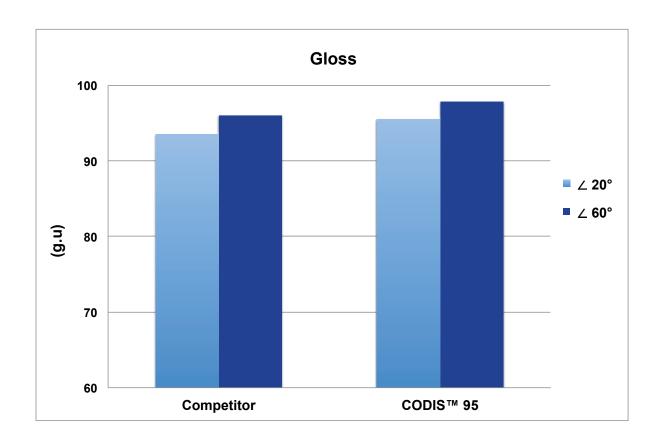
5.1 Solvent-based alkyd paint - Test formulation

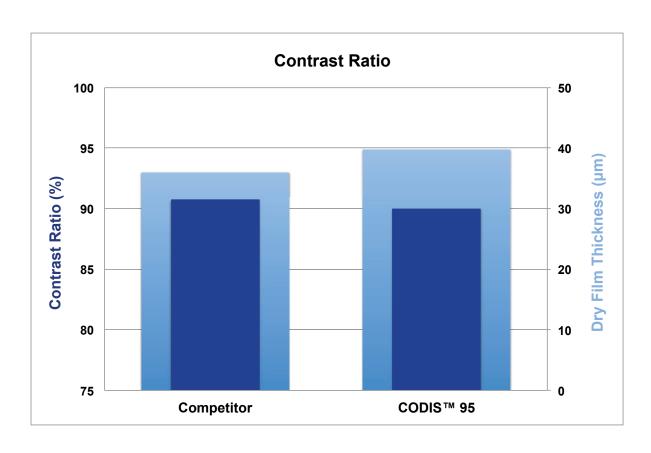
Component	Competitor	CODIS™ 95
Polikyd AS 652/75D	37.10	37.10
Bentone SD-1	0.10	0.10
Disperbyk 108	0.45	0.45
Titanium dioxide R-706	28.90	28.90
Calcium octoate 5%	1.30	1.30
Cobalt octoate 2%	1.05	1.05
Zirconium octoate 6%	1.35	1.35
White spirits (Solvent D40)	8.80	8.35
Xylene	3.05	2.05
Anti-skinning agent (MEKO)	0.25	0.25
Competitor amine	0.15	
CODIS™ 95		0.15
Water	17.50	18.95
Total	100.00	100.00

Characteristics	Competitor	CODIS™ 95	
	'		
Initial Flow time at 23°C (s)			
Stormer at 23°C (KU)	82.8	80.0	
Solvent for viscosity adjustment to 80 KU (%)	0.4		
Viscosities can			
Stormer at 23°C (KU)	80.0	80.0	
Solids content (%)	58.4	57.8	
Density at 23°C	1.210	1.208	
Solvent for viscosity adjustment to DIN4 70s (%)	3.0	3.3	
Viscosities for application by brush			
DIN4 23°C (s)	74	72	
Theoretical VOC (g/l)	299	299	

5.2 Gloss development and contrast ratio

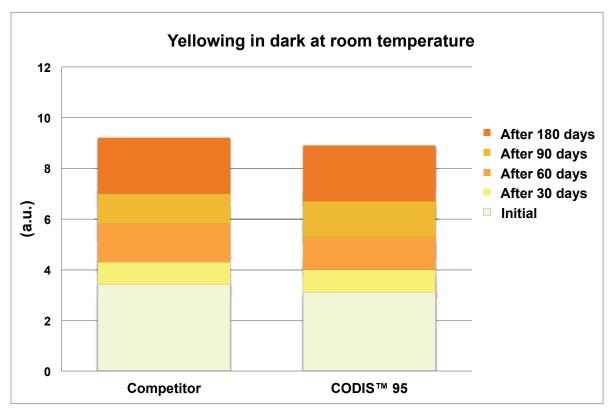
Incorporation of this amount of water using CODISTM 95 versus this well-known competitor results in higher gloss levels both at \angle 20° and \angle 60° whereas the contrast ratio is slightly lower at somewhat higher film thickness.





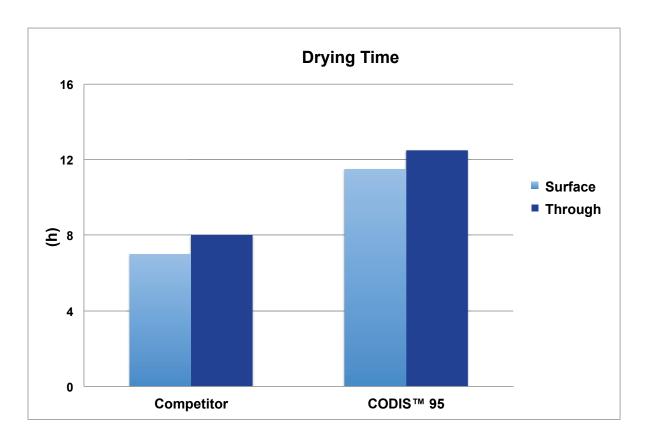
5.3 Yellowing in the dark

Upon aging in the dark CODIS™ 95 is less susceptible to yellowing compared to the competitor (see graph below). A similar trend is observed at 60°C.



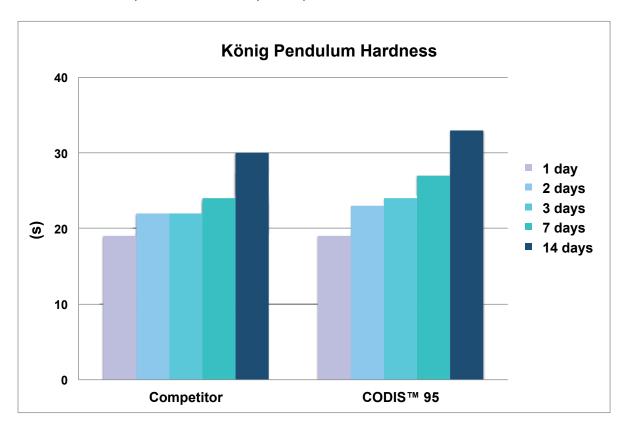
A prolonged drying time was observed for CODIS $^{\text{TM}}$ 95 which is mainly due to the slower evaporation rate and also inherent to a non-optimised formulation.

5.4 Drying time



5.5 König Pendulum Hardness

Remarkably, however, the development of the König pendulum hardness was positively affected by CODIS™ 95 in comparison with the competitive product.



6. Health, Environmental and Safety issues

For labelling of CODIS™ 95, CODIS™ BIO and ADDSPERSE ™ PH some physical data were compared with aminomethyl propanol (95% in water).

	CODIS™ 95	CODIS™ BIO	ADDSPERSE™ PH	AMP 95
Biobased carbon content, %	-	~34%	-	-
Free of environmental hazard label	✓	✓	✓	H412
Readily biodegradable	✓	✓	✓	✓
Free of human hazard label*	H314, H318 H332, H335	✓	H314, H318, H335	H315 H319
Hazardous pictogram - GHS	GHS05, GHS07	✓	GHS05, GHS07	GHS07
VOC content, % wt.	~45%	~0%	~27%	~95%

H332	Harmful if inhaled	H319	Causes serious eye irritation
H314	Causes severe skin burns and eye damage	H335	May cause respiratory irritation
H315	Causes skin irritation	H412	Harmful to aquatic life with long lasting effects
H318	Causes serious eye damage		

^{*} CODIS[™] 95: Label based on the sum of ingredients. CODIS[™] 95 has similar pH compared to AMP 95 (1% in water - *literature*): < 11.3 and a somewhat lower pKa: 9.54 vs 10.02.

Environmental information

CODIS™ 95, CODIS™ BIO and ADDSPERSE™ PH are expected to partition (preferentially locate) in water when released into the environment. Because of their water solubility and reactivity with other compounds, CODIS™ 95, CODIS™ BIO and ADDSPERSE™ PH biodegrade rapidly and are not likely to bioaccumulate in the aquatic food chain. Studies on a wide variety of freshwater fish show that these products have very low toxicity to fish.

CONTACT INFORMATION

ADDAPT Chemicals B.V.

Speltdijk 1 5704 RJ Helmond The Netherlands

Tel.: +31 (0)492 59 75 75 E-mail: info@addapt-chem.com http://www.addapt-chem.com

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