

Dibasic Esters

presented at

Paint Stripper Forum - Brussels

14 November 2005

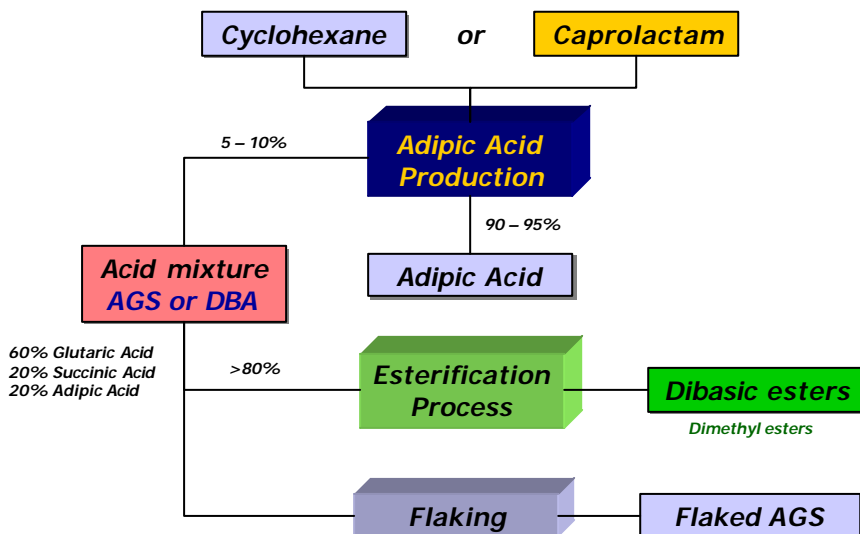
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Chairman

EASCR – European Association for Safer Coating Removal

Content

- How are dibasic esters produced?
- Product properties
- Dibasic esters in Paint Stripping in Europe
- Performance of DBE[®] paint strippers
- Cost factors related to alternative paint strippers
- Impacts following a possible DCM restriction

Sustainable Chemistry



Dibasic esters: benefits for formulators

- **Properties**
 - high solvency power
 - high boiling point
 - slow evaporation
 - high flash-point
 - low miscibility with water (favorable for waste water treatment)
 - high miscibility with most organic solvents
- **Safety to the environment**
 - low emission rate
 - not classified as VOC or Solvent at 20°C acc. 1999/13/EC
 - not listed on the Swiss VOC positive list
 - readily biodegradable
 - recyclable by vacuum distillation
- **Safety at the work place**
 - not corrosive
 - no skin sensitizer
 - non-flammable
 - mild and fruity odor
 - not classified as hazardous acc. to 7/548/EEC or 99/45/EC
 - not classified by IARC, NTP, ACGIH or OSHA as known, probable or possible human or animal carcinogen

Sources: various technical datasheets or publications

Hazard potential of dibasic esters

According to the ETVAREAD final report „Effectiveness of vapour retardants in reducing risks to human health from paint strippers containing dichloromethane“ from April 1, 2004 (page 46):

„... the risk potential of dibasic esters is not well understood and there remain uncertainties because dimethyladipate has dangerous properties:

- **In Germany dimethyladipate is „WGK 1“**
- **repeated exposure to dimethyladipate leads to „blurred vision“**
- **dimethyladipate is category 4 in the Swiss tox list.“.....**


Dibasic esters - Dichloromethane

Hazard potential of dibasic esters

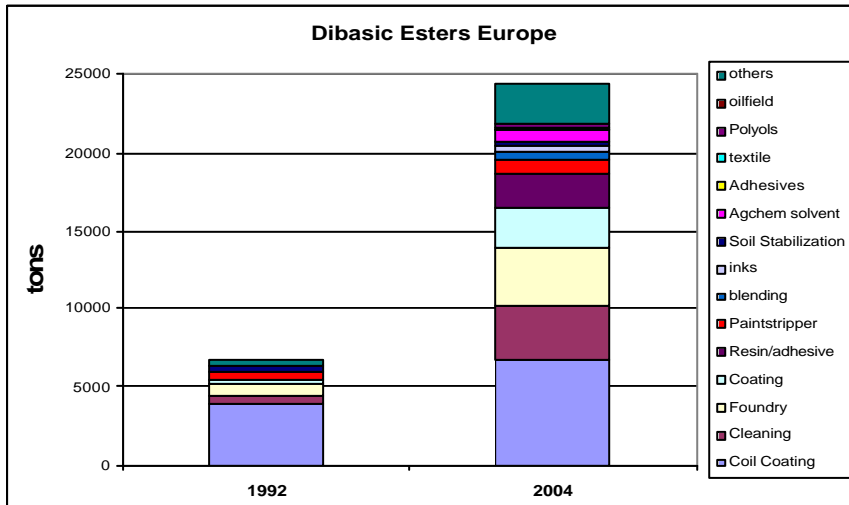
Composition of the substance	CAS-No	EC-No	Concentration
Dimethyl glutarate	1119-40-0	214-277-2	55 % - 65 %
Dimethyl adipate	627-93-0	211-020-6	10 % - 25 %
Dimethyl succinate	106-65-0	203-419-9	15 % - 25 %

	Dibasic Esters	Dichloromethane
Identification		
CAS-No.		75-09-2
EC-No.		200-838-9
EC-Index-No.		602-004-00-3
Physical and chemical properties		
Form at 20°C and 1013 hPa	liquid	liquid
Odour	sweetish	sweetish
Melting point (1013 hPa)	-20°C	43,7°C
Boiling point (1013 hPa)	196-225°C	40,67°C
Density (20°C)	1,092 g/cm ³	1,3283 g/cm ³
Vapour pressure (20°C)	0,08 hPa	475 hPa
Relative vapour density	-	2,9
Water solubility (20°C)	53 g/l	20 g/l
Flash point	103°C (cc)	-
Lower explosion limit	0,9 % (V)	13 % (V)
Upper explosion limit	8,0 % (V)	22 % (V)
Ignition temperature	370°C	556°C
Viscosity, dynamic	2,6 mPas (25°C)	0,43 mPas (20°C)
Toxicological Information		
Acute toxicity		
LD ₅₀ oral	8191 mg/kg (rat)	1600 mg/kg (rat)
LD ₅₀ dermal	> 2250 mg/kg (rabbit)	n.d.a.
LC ₅₀ inhalation	> 11 mg/l /4 h (rat)	76 mg/l/4 h (rat)
	Highest achievable concentration - no death	
Skin irritation	Slight irritations	Irritations
Eye irritation	Slight irritations	Slight
Sensitization	No sensitizing effects in animal experiments	No sensitizing effects in animal experiments
Mutagenic effects	No mutagenic effects in animal experiments	Mammalian cell test: negative Ames test: positive
Effects on reproductive toxicity	No effects on reproductive toxicity in animal experiments	No effects on reproductive toxicity in animal experiments

This comparison of hazard data of DBE and DCM was sent to the EU Commission on December 21, 2003 and is accurate from ECSA's point of view (15 April 2004)

Carcinogenic effects	No mutagenic effect in animal experiments	Carc. Cat. 3
Human experience	Harmful effects after contact with skin not known.	Skin and eyes: Irritation to eyes, skin, mucous membranes and respiratory tract. Repeated or prolonged contact may cause dermatitis.
	Inhalation: Temporary blurred vision (visible)	Inhalation: Severe narcotic effects, disorders of CNS (degenerative brain disease), liver (enlargement) and blood function (CO-Hb-formation) MAK: 350 mg/m ³ MAK: 100 ml/m ³
Daphnia toxicity	EC ₅₀ 48 h: 112-150 mg/l Daphnia magna	LC ₅₀ 96 h: 310 mg/l P. promelas LC ₅₀ 96 h: 220 mg/l L. machrochirus EC ₅₀ 48 h: 135-224 mg/l Daphnia magna IC ₅₀ 96 h: 360 mg/l S. capricornutum
Algal toxicity	n.d.a.	EC ₅₀ : 1000 - 2000 mg/l 15 min Microtox test 5 - 26 % after 28 days, not readily biodegradable (MTI test)
Bacterial toxicity	62,5 - 1000 mg/l 18 h RL LUBA	EC ₅₀ : 1000 - 2000 mg/l 15 min Microtox test 5 - 26 % after 28 days, not readily biodegradable (MTI test)
Biodegradability	87 % after 28 days, readily biodegradable (Closed bottle test)	
Partition coefficient n-Octanol/Water	n.d.a.	Log _P c: 1,3
Biological oxygen demand	50 mg/l WGK 1	n.d.a.
Water endangering class	WGK 1	WGK 2, No. 149, Annex 2 Annex 1
Classification 67/548/EEC	Not a hazardous substance according to 67/548/EEC	Xn 
R-phrases	-	R 40
S-phrases	-	S2-23-24/25-36/37
Transport information	Not classified as dangerous in the meaning of transport regulations	UN 1593, Dichloromethane, 6.1, PG III

The European market for dibasic esters is growing



Dibasic esters alone is not a paint stripper!

- **DBE & NMP**
 - 20% DBE
 - 10% NMP
 - 60% water
 - 9% others
 - 1% tenside
- **DBE & DMSO (dimethyl sulfoxide)**
 - 60% DBE
 - 27% DMSO
 - 6% dipropylene glycol methyl ether
 - 7% 1-(2-methoxy propoxy)
 - 2- propanol
- **DBE & others**
 - 60-70% DBE
 - 15-30% dipropylene glycolmonomethylether
 - 80% Water
 - 20% DBE
 - surfactant
- **80% DBE**
20% NMP
- **30% DBE**
60% ethoxyethylpropionate
10% NMP
- **50% DBE**
15% Gamma-butyrolactone
25% NMP
10% organic acid, thickener, etc.
- **40% DBE**
15% NMP
40% Aromatics 150
5% thickener, potassium oleate

- **1 Background and objectives**
 - Dichloromethane is a chlorinated solvent with a vapour pressure of 460,9 mbar (20 °C). It is known to be one of the strongest paint strippers available in common use.
 - *1st and 2nd sentence of the ETVAREAD report (1 April 2004) on page 1*
- **Conclusion**
 - It is clear that the Nitromors® All-Purpose (vapour retarded methylene chloride) formulation gives the quickest stripping, and has very low usage per squaremeter. The products that offer reasonable working times are generally based on „low flash solvents“ or NMP. Other technologies are generally very slow-acting.
 - *„Evaluation of Paint Strippers“ by the UKMC Paint Removers Group first distributed 26 April 2005*



Performance

Performance of DBE® paint strippers

- The performance of a paint stripper depends on the experience and competency of the formulator.
- Variation in the effectiveness of paint strippers is common whether based on DCM, dibasic esters, NMP or other solvents.
- A specific solvent does not automatically predict a performance or quality of a paint stripper.
- DBE® licensees try to differentiate their products by offering a performance that is equal to or better than leading DCM paint strippers, given the appropriate application method for alternatives.
 - Best performance of alternative paint strippers with longer penetration periods.

How effective are alternative paint strippers?

- Test performed at Invista Wilton, UK site.
- Paints treated had an age up to 20 – 30 years.
- Comparison test results were analyzed by 6-Sigma-technology.
- The coating engineer responsible for all painting work at the Invista Wilton site for the last 30 years participated in the Testing Team.
- Coatings included alkyd, acrylic, epoxy & polyurethane.
- Wood, plaster and metal substrated were selected.
- 12 samples were tested (9 based on dibasic esters incl. 7 with DBE®).
- Stripping after 3 different time periods:
 - 1 hour (to compare speed with “fast” DCM strippers)
 - 4 hours (apply in the morning, strip in the afternoon)
 - 18 hours (apply 1st day, strip 2nd day)
- Results recorded in AHP (Analytical Hierarchy Process)



Analytic Hierarchy Process



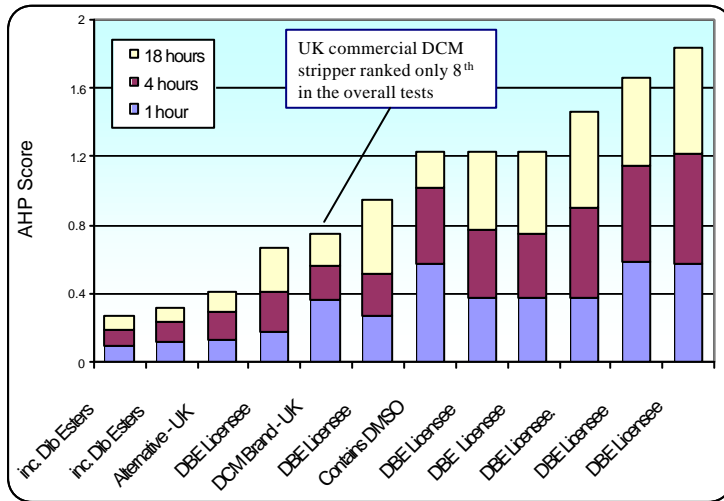
AHP for the 'Best' Paint Stripper in 24 hours on Alykd (oil based) paint on wooden substrate

9 - Extremely Better
8 -
7 - Very Strongly Better
6 -
5 - Strongly Better
4 -
3 - Moderately Better
2 -
1 - Same

Items	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6						Total	Avg
Sample 1	1	1/3	5	1/3	1/2	1/2	0.1	0.1	0.2	0.1	0.1	0.57	0.11
Sample 2	3	1	5	1/2	2	2	0.3	0.2	0.2	0.2	0.3	1.16	0.23
Sample 3	1/5	1/5	1	1/5	1/3	1/4	0.0	0.0	0.0	0.1	0.0	0.21	0.04
Sample 4	3	2	5	1	2	3	0.3	0.4	0.2	0.3	0.4	1.69	0.34
Sample 5	2	1/2	3	1/2	1	1/2	0.2	0.1	0.1	0.2	0.1	0.66	0.13
Sample 6	2	1/2	4	1/3	2	1	0.2	0.1	0.2	0.1	0.1	0.72	0.14
	11.2	4.5	23.0	2.9	7.8	7.3	1.0	1.0	1.0	1.0	1.0	5.0	1.00

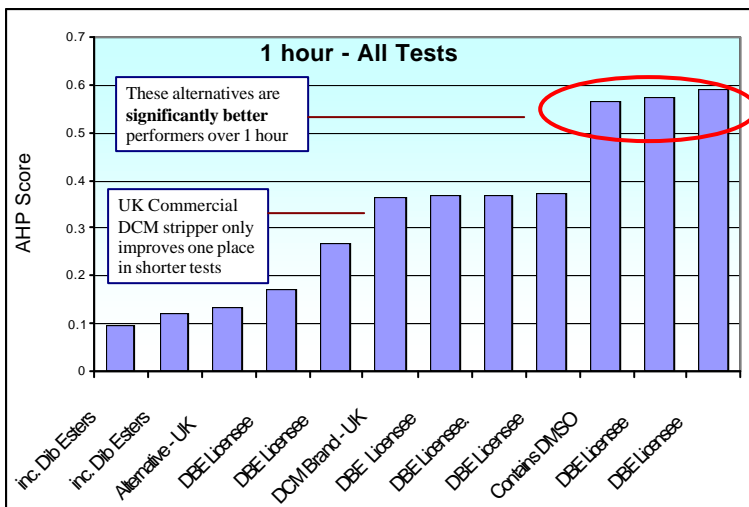
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Cumulative results of all tests

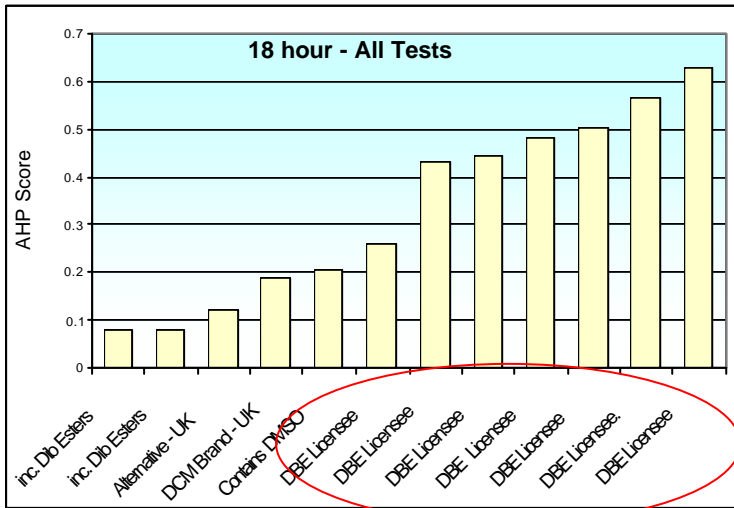


Most alternative strippers outperform DCM

Is DCM really the best performer over shorter periods?



Some alternatives are very effective over short periods



All DBE licensee strippers score better than any other sample

Cost of paint stripping
Personal protection

	<i>Dichloromethane-based Strippers</i>	<i>Dichloromethane-free Strippers</i>
Eye protection	If splashing is possible: goggles	If splashing is possible: goggles
Gloves made from	Fluoro caoutchouc	Polychloroprene, Nitrile caoutchouc
Skin protection	Fat free /low fat content ointment	Fat free /low fat content ointment
Respiratory protection during treatment		
- by hand	Self-contained respirators	-
- by spraying	Self-contained respirators	filter types: A1-P2
Protective clothing during treatment and cleaning	Disposable chemical protection clothing	Disposable chemical protection clothing
Cost	approx. 2.750.- Euros	approx. 75.- Euros

DCM-stripping is
37 x
more expensive



Source: GISBAU
 Industry Insurance of the
 German Construction
 Industry November 2005

Improved safety at lower cost!



Dichloromethane Dip-Tank

ECO DECAP Station®

COST		
Carbon steel tank: EUR 4.000,-	Investment for a 4m ³ tank	INOX steel tank with FLUSH DECAP MOVING® system and filtration section: EUR 16.300,-
Dichloromethane: EUR 8.000,-	Paint stripper	Bio Fluxaf Aqua® : EUR 25.600,-
EUR 88.000,-	Waste water treatment	n.a.
included	Filtration	Penetrated INOX tank with filter: EUR 1.200,-
EUR 100.000,-	TOTAL	EUR 43.100,-

DCM dip tank cost from Artisans Mag' no 21 Février 2005, p.12

Impacts following a possible DCM restriction

- Fewer severe paint stripping incidents.
- Lower cost to industry insurances and the society.
- Reduced non-compliance by retailers and decorators.
- Lower paint stripping cost per squaremeter through:
 - higher effectiveness
 - cheaper personal protection equipment
- Job creation in regional SME's.

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