TECHNICAL BULLETIN

DMPA®

DMPA® Dimethylolpropionic Acid in Waterborne PUDs for Coating Applications

$$\begin{array}{c} CH_2OH \\ | \\ CH_3 — C — COOH \\ | \\ CH_2OH \end{array}$$

CAS Number: 4767-03-7

DMPA® Dimethylolpropionic Acid is both a glycol and a carboxylic acid. By reacting the 2 primary hydroxyl groups of **DMPA®** with NCO groups of a diisocyanate to form urethane polymers, the tertiary carboxylic acid group can be easily formulated into the backbone of the polymer chain with no need to block the carboxylic group to prevent reaction. Thus, a resin formulated with **DMPA®** can be solubilised or dispersed in water by neutralisation of the unreacted carboxyl groups with ammonia, amines or other bases. In recent years, **DMPA®** has become the choice raw material for preparation of waterborne polyurethane dispersions (WB PUDs). It is well known that the introduction of – COOH, a polar group to the pre-polymer, helps improve coating adhesion and synthetic fibre dye receptivity.

Specifications

Property	Regular Grade
Hydroxyl Content, wt %	24.0 min
Neutralization Equivalent	141.0 max
Ash as Na_2O, wt %	0.03 max
Moisture, wt %	0.3 max
Water Insolubles, ppm	50.0 max
Colour, APHA	250 max

EUROPE
Charleston Road, Hardley,
Hythe, Southampton, Hampshire
SO45 3ZG UK
Call +44 2380 245 437

NORTH AMERICA
300 Brookside Avenue,
Building #23, Suite 100 Ambler,
PA 19002 USA

Call +1 215 773 9280 Toll

Free 888 519 3883

Email: PaintsandCoatings@geosc.com

www.geosc.com

GEO® SPECIALTY CHEMICALS

DMPA®

Currently, the most prevalent technology of synthesizing WB PUDs follows 4 basic steps:

1. Synthesis of NCO terminated pre-polymer
2. Neutralisation
3. Chain Extension
4. Dispersion

DMPA® is suitable for synthesizing WB PUDs for the preparation of both hard coating films and soft coating films. Depending on the design, such as choice of raw materials, ratio of the hard and the soft segment, degree of branching, molecular weight etc., waterborne urethane polymers with specific properties can be tailor-made to suit a specific purpose. **DMPA®** is the essential and most convenient material to impart water solubility or water dispersibility to the polymer.

In this bulletin, formulations of WB PUDs that provide a soft coating film, a hard coating film and an exceptionally tough (hard and flexible) coating film are presented. Also, features and benefits of using **DMPA®** for the preparation of WB PUDs are discussed. To assist the less experienced users of **DMPA®**, correct procedures for WB PUDs are provided. Precautions on how to prevent gel particle formation during urethane polymer synthesis are included in the notes.

Starting Point Formula

Table 1—DMPA based WB PUD, Soft Film Version

	Parts	Eq. Weight	Eq. #
Desmophen® S1015-55 [1]	259.20	1000	0.2592
DMPA® Dimethylolpropionic Acid [2]	21.20	67.05	0.3162
IPDI [3]	95.80	111.15	0.8619
Ethylene Diamine	4.32	30	0.1440
N-methyl-2-pyrrolidone [4]	97.00		
Triethylamine	13.58		
De-ionized Water (I)	391		
De-ionized Water (II)	108		
Total	**1000**		

1 Polyester polyol, 2000 M.Wt., OHV 55, product of Bayer

2 DMPA® Dimethylolpropionic Acid is a registered trademark of GEO Specialty Chemicals Inc

3 Desmodur® I, product of Bayer. Since IPDI is very reactive, no tin catalyst is needed. The presence of tin catalyst could promote the reaction of IPDI with water.

4 N-Pyrol, GAF Corporation

Procedures:

Part 1: Preparation of Isocyanate-terminated Pre-polymer

1. Charge Materials 1, 2 and 5 into a round bottom flask equipped with a temperature monitoring device, agitator, water-cooled condenser and inert gas sparge.

2. Heat with agitation to 85-90°C and add Material 3 in slowly with good agitation. Hold the batch @ 85°C for 3 to 4 hours. After that, check acid number (AN) and NCO content.

3. AN, at this time should be about 18.

4. NCO value is determined by the di-n-butylamine titration method.

5. When the theoretical NCO is reached (2.55%), drop the temperature to 60-65°C. The pre-polymer solution might need to be maintained at this temperature if the solution viscosity is too high for convenient transferring. If neutralisation, chain extension and dispersion do not follow immediately, cool down to room temperature to minimize the reaction between NCO and water.

6. Determine and record the properties of the pre-polymer solution, such as % NV, viscosity and AN. This pre-polymer is designed to have a theoretical NCO / OH ratio of 1.5, a % NV of 79.5 and an AN of ~18.

NB: For very small batches, reaction end point can be reached after 2 hours.

REVISION DATE: OCTOBER 2020

Procedures:

Part 2: Preparation of the WB PUD

1. Charge the pre-polymer (product of Part 1) into a suitable size stainless steel beaker.

2. Use a fast speed disperser of the type used for pigment dispersion.

3. Charge Material 4 (ethylene diamine) to a separate beaker. Add Material 8 (DI water II) into the beaker to dilute the amine.

4. Add Materials 6 and 7 in quick succession under fast speed agitation allowing the mixture to become homogeneous.

5. Add diluted Material 4 (the ethylene diamine solution prepared in step 3) slowly to the reaction beaker to maintain a constant vortex *.

6. Continue high speed mixing for 20 minutes. Check the viscosity of the dispersion. For easy filtration and handling, one may want to dilute the dispersion slightly with DI water.

7. Filter the dispersion using a 50μ pore-size polyester filter bag and discharge.

8. Determine the final properties of the dispersion, such as % NV, pH, Brookfield viscosity, etc.

*Adding ethylene diamine without dilution or adding it in too fast may result in a sudden viscosity increase; it can also cause gel particle formation.

This dispersion should have the following properties:

Resin Properties

	Results
NV %	39.4
pH	9.7
Brookfield Viscosity, cP	50 - 250 (12 cP @ 35% solids and 20°C)
Water / co-solvent ratio	82.6 / 17.4
VOC, grams / litre	215

REVISION DATE: OCTOBER 2020

Starting Point Formulation - DMPA based WB PUD, Hard Film Version I

Table 2—DMPA based WB PUD, Hard Film Version I

	Parts	Eq. Weight	Eq. #
Diexter-G IA66-120 [1]	172.80	500	0.3456
DMPA [2]	21.20	67.05	0.3162
Desmodur® W [3]	138.71	131	1.0589
2-methylpentamethylene diamine	17.25	58	0.2978
Dibutyl tin dilaurate [4]	0.02		
N-methyl-2-pyrrolidone [5]	180.00		
Triethylamine	13.58		
De-ionized Water (I)	97.75		
De-ionized Water (II)	358.69		
Total	**1000**		

1 Polyester polyol, Coim USA Inc.

2 DMPA® Dimethylolpropionic Acid, GEO Specialty Chemicals Inc.

3 Dicyclohexylmethane diisocyanate, Bayer

4 FASCAT tin catalysts, Atochem; for this formulation with Desmodur W, this catalyst is optional

5 N-Pyrol, GAF Corporation

Procedures:

Part 1: Preparation of the Isocyanate-terminated Pre-polymer

1. Charge materials 1,2,5 and 6 into a round bottom flask equipped with a temperature monitoring device, agitator, water-cooled condenser and inert gas sparge

2. Heat with agitation to 85°C, then add material 3 slowly. Hold at 85°C for 4 hours. After 4 hours check acid number (AN) and NCO content.

3. AN, at this time should be 17.2

4. NCO value is determined by the di-n-butylamine titration method.

5. When the theoretical NCO value is reached (3.24%), check the acid number and drop the temperature. Allow the solution to cool to 50-60°C.

6. Determine and record the final properties of the pre-polymer solution, such as % NV, viscosity and final AN. This pre-polymer is designed to have a theoretical NCO/OH ratio of 1.6, a % NV of 64.5 and an Acid Number of ~ 16

REVISION DATE: OCTOBER 2020

Part 2: Preparation of the WB PUD

1. Charge the pre-polymer (product of Part 1) into a suitable size stainless steel beaker.

2. Use a high speed disperser of the type used for pigment dispersion.

3. Charge material 4 (2-methylpentamethylene diamine) to a separate beaker. Add material 8 (DI water I) into the beaker to dilute the diamine.

4. Add materials 7 and 9 in quick succession, under high speed agitation allowing the mixture to become homogeneous.

5. Add the diluted material 4 (the diamine solution prepared in step 3) slowly to the reaction beaker. Add at a rate sufficient to maintain a constant vortex *.

6. Continue high speed mixing for 20 minutes.

7. Determine the final properties of the dispersion, such as % NV, pH, Brookfield viscosity etc...

* Adding the diamine without dilution or adding it too fast may result in a sudden viscosity increase or gel particle formation.

This dispersion should have the following properties:

Theoretical Properties

	Results
NV calculated %	36.4
pH	9.7
Brookfield Viscosity, cP	50 - 300
Water / co-solvent ratio	- 72 / 28
VOC, grams / litre	350

Starting Point Formulation - DMPA based WB PUD, Hard Film Version II

Table 3—DMPA based WB PUD, Hard Film Version II

	Parts	Eq. Weight	Eq. #
Diexter-G IA66-120 [1]	131.33	500	0.263
CHDM [2]	17.48	72	0.243
DMPA [3]	20.52	67.05	0.306
Desmodur® W [4]	162.11	131	1.237
2-methylpentamethylene diamine	18.53	58	0.319
Dibutyl tin dilaurate [5]	0.03		
N-methyl-2-pyrrolidone [6]	149.72		
Triethylamine	13.14		
De-ionized Water (I)	382.14		
De-ionized Water (II)	105.00		
Total	**1000**		

1 Polyester polyol, Coim USA, Inc.

2 1,4-cycolhexane di-methanol, Eastman Chemicals

3 DMPA® Dimethylolpropionic Acid GEO Specialty Chemicals Inc.

4 Dicyclohexylmethane diisocyanate, Bayer

5 FASCAT tin catalysts, Atochem; for this formulation with Desmodur W, this catalyst is optional

6 N-Pyrol, GAF Corporation

Procedures:

Part 1: Preparation of the Isocyanate-terminated Pre-polymer

1. Charge materials 1, 2, 3, 6 and 7 in to a round bottom flask equipped with a temperature monitoring device, agitator, water-cooled condenser and inert gas sparge. Heat to 85°C with agitation.

2. Add in material 4 (Desmodur® W) slowly with agitation and hold the batch at 85°C for 4 hours. After 4 hours, check acid number (AN) and NCO content.

3. AN, at this time should be about 17.

4. NCO value is determined by the di-n-butylamine titration method.

5. When the theoretical NCO value is reached (3.6%), check the acid number and begin to reduce the temperature. Allow the solution to cool to 50-60°C.

6. Determine and record the final properties of the pre-polymer solution such as %NV, viscosity and final AN. This pre-polymer is designed to have a theoretical NCO / OH ratio of 1.525, a %NV of 68.9 and AN of ~ 18.

REVISION DATE: OCTOBER 2020

Part 2: Preparation of the WB PUD

1. Charge the pre-polymer (product of part 1) into a suitable size stainless steel beaker.

2. Use a high speed disperser of the type used for preparing pigment dispersions.

3. Charge material 5 (2-methylpentamethylene diamine) to a separate beaker. Add material 9 (DI water II) into the beaker to dilute the amine.

4. Add materials 8 and 10 in quick succession under high speed agitation allowing the mixture to become homogeneous.

5. Add the diluted material 4 (the diamine solution prepared in step 3) slowly to the reaction. Add at a rate sufficient to maintain a constant vortex. (Adding this material in too fast may result in a sudden viscosity increase or gel particle formation).

6. Continue high speed mixing for 20 minutes.

7. Determine the final properties of the dispersion, such as % NV, pH, Brookfield viscosity etc..

This dispersion should have the following properties:

Theoretical Properties	
	Results
NV calculated %	36.3
pH	~ 9.7
Brookfield Viscosity, cP	15 (@ 25°C and 35% NV)
Water / co-solvent ratio	- 72 / 28
VOC, grams / litre	346

REVISION DATE: OCTOBER 2020

Properties of DMPA based WB PUD & Clear Coating Films

The results of the dispersions and clear coating films of the above 3 formulations are summarized in the following table. Two excellent commercial WB PUDs, Sancure® 825 of Noveon and Spensol® L-512 of Reichhold are used as controls. All samples were air dried for 7 days before testing, unless otherwise stated. All films were applied at 0.15 mm wet film thickness.

Table 4—Film Performance

	GEO Hard II	GEO Hard I	GEO Soft	Sancure® 825	Spensol® L-512
Dry Times Hrs.					
Set	0.5	0.25	0.25	0.25	0.5
Through	1.25	1.0	0.5	0.5	0.75
Hard	2.0	2.0	3.25	1.0	2.0
Sward Hardness					
1 day	22	22	6	24	26
3 days	32	24	6	30	32
7 days	40	28	6	28	38
Tukon Hardness					
7 days	6.27	4.22	0.87	7.62	4.56
Impact Resistance lb / in, Reverse / Direct					
	160 / 160	160 / 160	160 / 160	160 / 160	160 / 160
Shore A Hardness					
	(96)	90	70	(96)	(94)
Shore D Hardness					
	64	58	(31)	66	64

REVISION DATE: OCTOBER 2020

Mechanical Properties

All the tensile specimens are 0.2 - 0.5 mm thick

Table 5—Mechanical Properties

	GEO Hard II	GEO Hard I	GEO Soft	Sancure® 825	Spensol® L-512
Tensile properties, psi	5748	7587	4418	3891	3208
Elongation, %	158	305	657	172	55
Modulus @ 10%, psi	4596	2780	363	3059	4197
Modulus @ 100%, psi	5035	3962	775	3262	sample broke
Modulus @ 300%, psi	sample broke	sample broke	1399	sample broke	sample broke
Tear strength, psi	196	174	366	95	92

Chemical Resistance

Table 6—Chemical Resistance

	1 N NaOH			1 N HCl		
	1hr	4hr	24hr	1hr	4hr	24hr
GEO Hard II	no effect	no effect	no effect	no effect	no effect	no effect
GEO Hard I	no effect	no effect	hazing [1]	no effect	no effect	no effect
Sancure® 825	no effect	no effect	hazing	no effect	no effect	no effect
GEO Soft	removal	removal	removal [2]	no effect	no effect [3]	no effect [3]
Spensol® L-512	no effect	no effect	removal	no effect	no effect	no effect

1 The GEO Hard I sample had blister spots to the aluminium substrate

2 The GEO Soft sample failure was considerably worse than the Spensol® L-512

3 The GEO Soft sample displayed a slight haze-ring where the HCl drop was placed

REVISION DATE: OCTOBER 2020

Household Chemical Resistance 24 hours

Table 7—Household Chemical Resistance 24 hours					
Sample	Ketchup	Mustard	Shoe Polish	Lipstick	Crayon
GEO Hard II	no effect	heavy	moderate [1]	no effect	no effect
GEO Hard I	faint	heavy	moderate / heavy [1]	slight	faint
Sancure® 825	no effect	moderate	moderate [1]	no effect	no effect
GEO Soft	faint	very heavy	very heavy [1]	slight	none
Spensol® L-512	no effect	no effect	no effect	no effect	no effect

1 The black shoe polish left yellow stains

Water Resistance 24 hours

Table 8—Water Resistance 24 hours	
	Results
GEO Hard II	no effect
GEO Hard I	hazing - blushing
Sancure® 825	no effect
GEO Soft	heavy blushing [1]
Spensol® L-512	#7 blisters medium dense [2]

1 Some softening of the film was noted

2 Blisters were localised in patches and were not throughout the whole panel

REVISION DATE: OCTOBER 2020

Other Physical Properties

Table 9—Other Physical Properties

Sample	Pencil Hardness	Adhesion	Taber Abrasion (wt. loss)	Taber Abrasion (wt. loss)
GEO Hard II	2H	5B	Not determined	Not determined
GEO Hard I	F	5B	0.00185	0.00565
Sancure® 825	H	5B	0.0195	0.0323
Spensol® L-512	H	5B	0.0026	- [2]
GEO Soft 1	-	5B	0.0075	0.0151

1 The GEO Soft formulation is easily marred but the indentations self-heal. This makes pencil hardness difficult to quantify.

2 The weight loss at 1000 cycles was less than that of 500 indicating that the film was picking up the abrasion media (weight loss = 0.0017).

Conclusions

1. Features & Benefits of Using DMPA in WB PUD

From the 3 examples above, one can summarize the benefits of using DMPA in waterborne polyurethane dispersions. The same benefits can be realized when DMPA is used in WB PUDs for adhesive and ink applications.

Features & Benefits

* Diol with non-reactive carboxylic group, neopentyl structure	* Easy to introduce free acid groups to polymer chain to impart water dispersibility * Forms stable urethane dispersion * Works wee with all types of isocyanate * COOH improves adhesion for coating film
* Economical to use	* Only need 4-6% in dispersion for coatings, 2-3% in dispersions for adhesives
* Easy to use	* No need to protect the acid group at 65-90° C, the reaction temperature range for OH and NCO groups
* Safe to handle	* Very low toxicity, LD50 > 5000mg / kg, cleared for adhesives used under FDA regulations

REVISION DATE: OCTOBER 2020

2. Composition determines the physical properties of the polyurethane dispersions and coating performances of the films

The above work showed that composition of the urethane polymers is the major factor that determines physical properties of the polymer solution and film properties. Waterborne polyurethane resins can be tailor-made to suit specific applications in coatings.

3. DMPA can be used to synthesize WB PUDs for preparing both soft and hard films

The hardness and the flexibility of a urethane polymer is determined by the ratio of the hard segments and the soft segments of the polymer. Since the quantity of DMPA used in WB PUDs is usually very small, its presence is not a determining factor of the urethane polymer hardness. It is however essential to the water dispersibility of the polymer.

As demonstrated in the formulations above, DMPA is suitable to make WB PUDs for both soft and hard coatings.

Registration & Regulatory Information: Please refer to the safety datasheet.

Handling & Storage: DMPA® is classified as "DOT not regulated" by the US Department of Transportation and requires no special labelling for shipment. The Harmonized Tariff Code is 2918.19.40

DMPA® should be stored in a clean, dry area, following good warehousing practices.

Shelf-life: DMPA® has a minimum shelf of not less than 3 years if stored in its original unopened container and under normal storage conditions.

Miscellaneous: **DMPA®** is packaged in 250lb fibre drums, 50lb and 25kg multi-wall paper bags with HDPE liners and 500kg super sacks with LDPE liners.

REVISION DATE: OCTOBER 2020

GEO® SPECIALTY CHEMICALS